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ALUMINUM SURFACE TREATMENTS FOR
SIMPLIFIED ADHESIVE BONDED REPAIR

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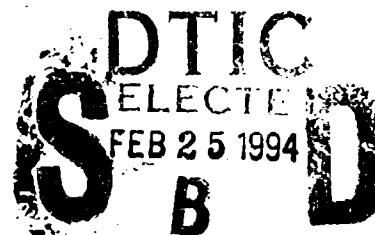
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CAPE COD RESEARCH, INC
BUZZARDS BAY, MA

FEBRUARY 1989

FINAL REPORT FOR 05/01/88-04/01/89

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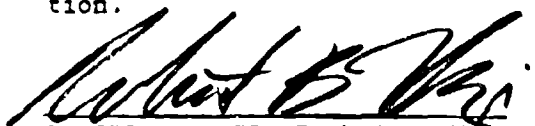AIR FORCE SYSTEMS COMMAND
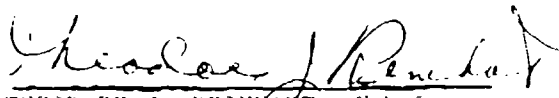WRIGHT PATTERSON AFB OH 45433-7734

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A new method for simplified adhesive bonded repair of aluminum structures was developed as a possible replacement for current pre-bond surface treatments. A series of adhesive primers, based on novel polyepoxide derivatives were prepared and tested on aluminum aircraft alloys which had been pretreated by a variety of different techniques. Experimental formulations were identified which when applied to surfaces that had been abraded by a new process developed by the Air Force yielded adhesive bonds with the initial strength and durability of those prepared by FPL etch pretreatment and commercial primers.

The Air Force has been searching for viable replacements for the hazardous and cumbersome pre-bond surface treatments currently employed for the field repair of aircraft structures. There is also a need to a replace anti-corrosion primers based on hexavalent chromium compounds because of their toxicity. The basic approach in this study involved the development of primer resins which have a high affinity for pretreated aluminum surfaces and the various adhesives employed in bonded repair. The primer resins were tailored to adhere well to the substrates and prevent water from entering the bond line. Certain experimental primer formulations were found to work exceptionally well on Al 2024-T3 alloy. Factors which were found to affect the adhesion performance were: pre-prime surface treatment, structure of primer resins, and primer cure conditions.

1.0 INTRODUCTION

One of the most important steps in the adhesive bonding process is adherend surface preparation. Commonly used surface treatments for aluminum alloys include solvent wiping, vapor degreasing, abrasive cleaning such as grit blasting for removing oxide coatings and loose particles, anodization, and chemical etching.[1] Many of these treatments require sophisticated equipment and the use of hazardous chemicals to achieve the desired surface effects and thus are difficult to perform in the field.

The industry standard for many years for surface treating aluminum alloys has been the FPL (Forest Product Laboratories) etch. This involves the following steps: degrease, alkaline clean, rinse, and exposure to a sodium dichromate-sulfuric acid solution at 68°C for 15-30 minutes.[2] This procedure leaves a surface coating of aluminum oxide whose chemistry and morphology promote strong adhesive bonding. A modification of this technique involves using a paste form of the chromic acid etchant. This allows the selective etching of parts where it is impractical to totally immerse them in etching solution. These methods, however, require strong oxidizing agents like chromic acid which is highly corrosive and potentially carcinogenic.

Another surface treatment which has gained wide acceptance and has been thoroughly evaluated by the Air Force is phosphoric acid anodization (PAA). In this technique, the degreased and abraded adherends are typically connected to a DC power supply, placed in a 12 % solution of phosphoric acid and anodized at 10 volts for about 23 minutes at about 80°F. Upon completion of the PAA, the parts are immediately rinsed to prevent resolution of the anodized layer. A non-tank PAA treatment has been developed by Boeing for repair procedures where immersion of parts is undesirable or impossible. In this procedure the phosphoric acid electrolyte is gelled with a fumed silica thixotropic agent, applied to the bonding area with a screen electrode, held in place with gauze and anodized in the usual manner.[3] The main advantages of the PAA process are the durability of the bonds obtained and the environmental acceptability. PAA however requires trained personnel and somewhat cumbersome equipment to achieve the desired results.

The chromic acid etching and phosphoric acid anodization procedures have been shown to produce microporous aluminum oxide surface morphologies which are believed to mechanically interlock with adhesives resulting in stronger bonds. The desired aluminum oxide structure is a hard crystalline form known as boehmite. It has been reported that aging of FPL-etched Al2024-T3, in humid atmosphere, transformed the thin boehmite film to a thicker weak bayerite film which has been postulated to cause bond degradation. Another approach to surface preparation which only requires etching aluminum

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adherends in concentrated sodium hydroxide was reported to achieve bond strengths and durability comparable with those prepared by standard FPL etch treatment[4]. These processes, however, do not address the problem of how to keep environmental moisture away from the sensitive aluminum oxide layers so that bond integrity can be maintained.

The principal method of protecting the fragile anodized aluminum surfaces before adhesive bonding is by coating with a corrosion inhibiting primer. Hexavalent chromate corrosion inhibitors have been used extensively for this purpose. The Air Force employs epoxy primers containing $SrCrO_4$ for both adhesive bonded repair and for undercoating aluminum structures. Chromates inhibit corrosion by retarding the anodic electrochemical reaction. Strong oxidizers such as these promote passivation of the metal surface through the formation of metal oxide layers.[5] While chromate corrosion inhibitors perform quite well they are toxic to both personnel and the environment. There has been a great deal of effort focussed on finding a replacement for these compounds for both adhesive and protective coatings applications.

One alternative to using chromate-filled primers on aluminum for promoting adhesion durability involves forming strong covalent bonds with the adherend surface through the use of an unpigmented polymer. The resin would, in principle, bond strongly to both metal adherends and most classes of structural adhesives and prevent water from penetrating into the bond line.

2.0 TECHNICAL APPROACH

The overall approach consists of chemically and mechanically pretreating the aluminum adherend surfaces and priming with a proprietary copolymer resin which has a strong affinity for the treated surface. Two methods for pretreating the aluminum were evaluated. The first was an alkaline silicate etch and the second, developed at Wright-Patterson AFB involved wetsanding with an aqueous solution of hydrolyzed silane coupling agent. The pretreated surfaces were then coated with a variety of different primer formulations based on phosphate-modified epoxy-silicone copolymers. The primed specimens were bonded with a commercial rubber-modified epoxy film adhesive and evaluated for initial adhesive strength by lap shear tests and bond durability by wedge tests.

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Adhesion test specimens were also prepared by the FPL surface treatment and priming with a commercial corrosion inhibiting primer and tested as controls. Surface analyses were performed before and after the adhesion tests to determine the effects of the different treatments and as part of the failure analysis. Fourier Transform Infrared (FTIR) spectroscopy, Electron Spectroscopy for Chemical Analysis (ESCA), and Scanning Electron Microscopy (SEM) were the techniques employed to study the chemical and morphological properties of the adherend surfaces.

3.0 EXPERIMENTAL PROGRAM

3.1 Preparation of Phosphate-Modified, Epoxy-Silicone Copolymers

Phosphate-Modified Epoxy Resin

A key element in this primer system is a new epoxy-phosphate resin, experimentally available from Dow Chemical Co. The phosphates, which have a strong affinity for polar surfaces, are covalently bound in the epoxide polymer backbone. This unique feature was designed to improve the overall adhesive properties of the primers. A generalized structure of the epoxy-phosphate is shown below:
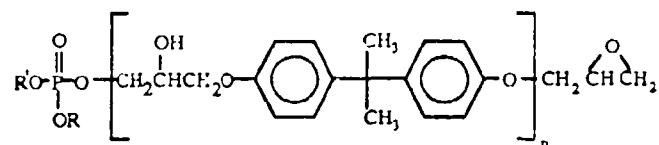
R, R' = H, alkoxy, bisphenol or bisphenol epoxy

Silicone Crosslinking Reactions

The polysiloxanes chosen contain reactive amine and alkoxysilane groups which serve as both crosslinking sites and potential bonding sites to polar surfaces. The combination of reactivity and fluidity exhibited by the polysiloxanes should imbue the primer with excellent surface wetting properties. The flexible siloxane polymers, when covalently crosslinked into the epoxy-phosphate matrix should improve the impact resistance and the adhesive peel strength of the material. Silicones also have the desirable property of migrating to the copolymer-air interface where their water repellency may hinder hydrolytic degradation at the exposed bond line area.

Copolymers of the epoxy phosphate resin and polysiloxanes were formed by the reaction of the epoxy resin, hydroxy-terminated polysiloxanes, polyamides, and alkoxysilane crosslinking agents. The

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approach uses a combination of RTV silicone and conventional epoxy cure chemistry. An amine-functional alkoxysilane, 3-aminopropyltrimethoxysilane serves as the link between the epoxy and siloxane segments of the copolymer. The amine-functional alkoxysilanes are well known as adhesion promoters for bonding organic polymers to a variety of substrates. Their inclusion in these formulations is two-fold: to serve as covalent bridging agents between the epoxy and siloxane and to promote better adhesive interactions between primer and substrate. The titanium (IV) butoxide-catalyzed cure of polysiloxane resins can be represented as follows:
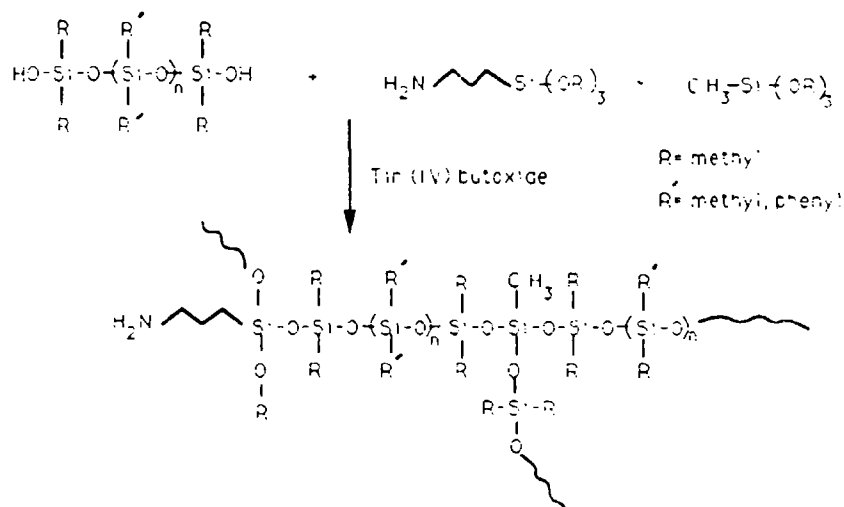
Figure 3.1. Polysiloxane Crosslinking Reaction

Ambient Temperature Curing Silicone-Epoxy-Phosphate Compositions

A series of epoxy phosphate-silicone copolymers was synthesized to determine the effect of different silicone levels. Copolymers were prepared from the epoxy phosphate resin, cycloaliphatic amine curing agent (Ciba-Geigy XUHY-265), 3-aminopropyltriethoxysilane, and silanol-terminated polydimethylsiloxane with the level of polysiloxane varied between 0-15 weight percent. All of the compositions cured at room temperature within 24 hours to hard plastics. It was noted that as the silicone content was increased, the optical clarity of the cured films diminished. This was most likely due to phase separation between the polysiloxane and polyepoxide segments of the copolymer.

The chemical reactions necessary for properly crosslinking the copolymer resins proposed in this study, namely the reaction between amines and epoxides and between alkoxysilanes and silanols were monitored by FTIR. Solutions of the reagents in methylene chloride were sprayed as thin coatings on aluminum foil and allowed to air dry at ambient temperature for 30 minutes. The coated foil was mounted in a Multiple Internal Reflectance(MIR) attachment for the FTIR and an initial IR spectrum

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taken. The samples were heated at temperatures between 25-100°C for different periods and the extent of cure monitored by FTIR.

It was found that the copolymers could be effectively cured as measured by the disappearance of IR absorbance bands corresponding to epoxide and alkoxysilane groups (916 and 798 cm^{-1} respectively) by heating for one hour at 60°C. IR spectra showing these changes with curing conditions are provided in Appendix 1.

3.2 Aluminum Substrate Surface Treatments

Adherends composed of aluminum alloys 2024-T3 and 7075-T6 were treated by several methods before priming and adhesive bonding. The three basic pretreatment methods evaluated in this study were alkaline etching with a sodium metasilicate solution, the modified Windecker method which involves wetsanding with silane coupling agents and primer formulations, and the FPL etch which was used as a control. The original Windecker method, developed by Dr. Leo Windecker is described as mechanical abrasion of the adherend surface under a protective layer of the liquid adhesive in combination with a silane wetting agent.[3] This process has been successfully modified by Purcell[6] where an aqueous solution of the silane is used instead of an adhesive solution during abrasion. This is followed by priming with another silane coupling agent and the resulting adhesive bonds were reported to have excellent durability.

Each of the aluminum surface treatments is described below and given a label with which it will be referred to elsewhere in this report. Note: all aluminum surface treatments were preceded by a degreasing step where the surfaces of the adherends were thoroughly rinsed with methylene chloride and wiped with a paper towel saturated with the solvent.

FPL Chromic Acid Etch (FPL)

Substrates were etched at room temperature (70°F) in an alkali-silicate solution consisting of 19 % sodium metasilicate, 1 % sodium hydroxide, 1 % phosphate detergent, and 79 % deionized water for 5 minutes, rinsed with deionized water, etched at 60°C chromic acid solution consisting of 2 % sodium dichromate, 24 % concentrated sulfuric acid and 73 % deionized water for 12 minutes, thoroughly rinsed in deionized water and dried in an air circulating oven at 60 °F for 2 hours.

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Alkali-Silicate Etch (Sil-1)

Substrates were etched in an alkali-silicate solution based on 19 % sodium metasilicate,1 % sodium hydroxide,1 % phosphate detergent,and 79 % deionized water at room temperature for 5 minutes, rinsed thoroughly with deionized water, and dried in an air circulating oven at 60 ^{O}F for 2 hours.

Alkali-Silicate Etch With Pre-Priming (Sil-2)

Substrates were first etched in alkali-silicate solution by the Sil-1 process, allowed to cool to room temperature, and then pre-primed with a 1 % aqueous solution of hydrolyzed silane coupling agent 3-glycidoxypropyltrimethoxysilane (Dow-Corning Z-6040). The Z-6040 was allowed to hydrolyze in solution for one hour at room temperature before being sprayed onto the adherends. The pre-primed samples were dried in an air circulating oven at 60°F for two hours.

Modified Windecker Surface Treatment (WND-1)

Substrates were wetsanded with DEPR/CAAA a 1` % primer solution composed of a stoichiometrically balanced mixture of Dow epoxy phosphate resin (DEPR) and a cycloaliphatic amine adduct curing agent (CAAA, Ciba-Geigy XUHY-265) in methylene chloride. A fine grade of emery cloth was used and after sanding the surfaces were cleaned free of abrasive by wiping with a cloth saturated with the wetsanding solution. The treated adherends were allowed to dry at room temperature for ore hour.

Modified Windecker Surface Treatment (WND-2)

Substrates were wetsanded with a 1% primer solution composed of a stoichiometrically balanced mixture of DEPR, CAAA, a silanol-terminated polydimethlysiloxane fluid having an average silicone block length of 7, and the silane coupling agent, 3-aminopropyltriethoxysilane (GAPTES,Petrarch Systems) in methylene chloride. A fine grade of grade of emery cloth was used. After sanding, the surfaces were cleaned free of abrasive by wiping with a cloth saturated with the wetsanding solution. The treated adherends were allowed to dry at room temperature for one hour.

Modified Windecker Surface Treatment (WND-3)

Substrates were wetsanded with a 1 % solution of Z-6040 in tetrahydrofuran to which was added a small amount of water (stoichiometric with respect to the total number of alkoxysilane groups). The wetsanding

solution was allowed to hydrolyze at room temperature for one hour before use. A fine grade of grade of emery cloth was used. After sanding, the surfaces were cleaned free of abrasive by wiping with a cloth saturated with the wetsanding solution. The treated adherends were dried in an air circulating oven at 60°F for two hours.

Modified Windecker Surface Treatment (WND-4)

Substrates were wetsanded with a 1 % solution of Z-6040 in water. The Z-6040 was allowed to hydrolyze in solution for one hour at room temperature before wetsanding. A fine grade of emery cloth was used. After sanding, the surfaces were cleaned free of abrasive by wiping with a cloth saturated with the wetsanding solution. The treated adherends were dried in an air circulating oven at 60°F for two hours.

Modified Windecker Surface Treatment (WND-5)

The procedure described for method WND-4 was followed except that GAPTES was substituted for Z-6040.

Modified Windecker Surface Treatment (WND-6)

The procedure described for method WND-4 was followed except that 1 % of the tetrasodium salt of ethylenediaminetetraacetic acid (Aldrich) was added to the wetsanding solution.

3.3 Adhesive Primer Development and Application

A variety of experimental adhesive primer formulations were prepared and applied to pre-treated aluminum adherends prior to adhesive bonding. A commercial adhesive primer, BR-127 (kindly furnished by American Cyanamid) was also employed as a control treatment for FPL-etched samples.

3.3 Experimental Primer Formulations

A series of experimental adhesive primers were prepared from epoxy resins, silicone polymers, amine curing agents, titanium alkoxide catalyst and methylene chloride solvent and applied to aluminum substrates treated by the methods described above. Ten weight percent solids formulations were prepared by dissolving the primer components together in methylene chloride. The primer solutions

were normally used within an hour of preparation although they were not observed to change in appearance for over 24 hours. After 48 hours, however, precipitation of gel-like material was noted. Table 3.1 lists the compositions of the experimental primers evaluated in this program.

Table 3.1. Experimental Primer Compositions

Primer Code	Silicone Resin	Silicone Wt. %	GAPTES Wt. %	Amine Adduct	Amine Wt. %	Epoxy Resin	Epoxy Wt. %	Si-OR Si-OH
A1	N. A.	0	0	CAAA	24	DEPR	76	N. A.
A2	D7PDMS	1	0.5	CAAA	23.5	DEPR	75	0.67
A3	D7PDMS	5	1.3	CAAA	21.7	DEPR	72	0.67
B1	N. A.	0	0	MAAA	15	DEPR	85	N. A.
B2	D7PDMS	5	4	MAAA	12	DEPR	79	2.00
B3	D7PDMS	10	8	MAAA	9	DEPR	73	2.00
B4	D7PDMS	15	12	MAAA	6	DEPR	67	2.00
B5	D23PDMS	5	1	MAAA	14	DEPR	80	2.00
B6	D12PDPDMS	5	2.4	MAAA	13.4	DEPR	79.2	2.00
B7	N. A.	0	4	MAAA	13	DEPR	83	N. A.
B8	D7PDMS	5	1	MAAA	14	DEPR	80	0.67
B9*	D7PDMS	5	1	MAAA	14	DEPR	80	0.67
B10	D56PDMS	5	0.6	MAAA	14.4	DEPR	80	2.00
B11	D7PDMS	5	4	TAAA	18	DEPR	73	2.00
C1	D7PDMS	5	4	MAAA	19	DER	72	2.00
D1**	N. A.	0	0	X1-6100	25	N. A.	0	N. A.

DxPDMS = Polydimethylsiloxane, silanol terminated, where x = no. siloxy units (Petrarch Systems)

DxPDPDMS = Polydiphenyldimethylsiloxane, silanol terminated, where x = no. siloxy units (Petrarch Systems)

CAAA = Cycloaliphatic amine adduct (XUHY-265, Ciba-Geigy)

MAAA = Modified aromatic amine adduct (XB-3075, Ciba-Geigy)

TAAA = Toughened aromatic amine adduct (XU-264, Ciba-Geigy)

GAPTES = 3-aminopropyltriethoxysilane (Silar Laboratories)

DEPR = Dow phosphate-modified epoxy resin (XU 71814.00L, Dow Chemical)

DER = Bisphenol A epoxy resin (DER-331, Dow Chemical)

X1-6100 = Experimental phenyldimethoxyaminopropylsilane coupling agent (Dow Corning)

Si-OR = No. moles alkoxysilane groups from GAPTES

Si-OH = No. moles silanol end groups from D_xPDMS or D_xPDPMS

* = Primer B10 filled with 10 wt. % neutral aluminum oxide (-200 mesh, alpha form, Alfa Ventron)

** = Primer D1 composed of 25 wt.% X1-6100 in isopropanol

N. A. = Not Applicable

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Primer Application Methods

Primer formulations were sprayed onto aluminum substrates using an air compressor and hand-held spraygun. The aluminum samples were cooled to room temperature before priming. The spray technique consisted of using two cross coat spray passes to give smooth and uniform coverage. The dry primer thickness was maintained between 0.0004 and 0.0006 in.

Samples coated with experimental primers were either dried in air at room temperature for 30 minutes and at $65^{\circ}C$ for one hour or at room temperature for one hour. When BR-127 primer was used the primed samples were dried at room temperature for 30 minutes and cured at $120^{\circ}C$ for 30 minutes.

Primed Surface Analysis by SEM and ESCA

Selected samples were analyzed by Scanning Electron Microscopy (SEM) and Electron Spectroscopy for Chemical Analysis (ESCA) to determine surface chemical characteristics and morphology. The analyses were performed by Photometrics, Inc. of Woburn, Massachusetts.

3.4 Adhesion Testing

The experimental and commercial primers described above were applied to aluminum alloys 2024-T3 and 7075-T6 after pretreatment. The primed adherends were used to assemble wedge test and lap shear specimens.

Preparation of Adhesion Test Specimens

Suitably primed lap shear test coupons and wedge test panels were adhesively bonded with FM 123-2 supported film adhesive (kindly supplied by American Cyanamid). FM 123-2 is a nitrile rubber-modified, one-part epoxy adhesive film on a polyester mat and is designed for structural bonding applications. The grade used for this study had a nominal thickness of 0.011 in. and was stored in a freezer kept below $0^{\circ}F$. Before applying, the adhesive was allowed to warm to room temperature.

Lap shear specimens were prepared individually from aluminum coupons having dimensions 4 by 1 by 0.062 in. The primed coupons were adhesively bonded by fixing a 1 by 0.5 in. piece of film adhesive at the end of one coupon and placing the other on top. Two more coupons and 0.01 in. thick Teflon film spacers were placed on either side of the specimen to give a level structure and maintain the bond line thickness during cure. The specimen assemblies were placed between the platens of a heated Carver

Laboratory Press. A pressure of 50 psi was maintained during the adhesive cure cycle which consisted of 60 minutes of heating from room temperature to 225°F followed by 90 minutes at 225°F. After cooling, the assemblies were taken apart to yield the lap shear joints. Any adhesive which flowed to the outer edges of the joints was removed with a razor blade before testing.

Wedge test specimens were generally prepared from two pretreated and primed aluminum plates with initial dimensions 6" X 6" X 0.125". A piece of film adhesive with dimensions 6" X 5" would be placed over one aluminum plate, leaving at one end an uncovered area measuring 1" X 6". A 0.01" X 1" X 8" piece of Teflon film would be placed over the end space and the other plate would be placed on top. The adhesive was cured by heating under pressure as described above for the lap shear specimen assembly. After cooling, the Teflon spacer was removed, the sandwich assembly marked off into five, 1"-wide specimens and the piece cut with a bandsaw into five, 1" X 6" wedge test specimens. The two, 0.5"-wide end pieces were also cut off and discarded. The edges of the specimens were filed smooth before testing.

Initial Adhesive Strength (Lap-Shear) Testing

The lap shear tests were performed at room temperature on a Tinius Olsen Super "L" Universal Testing Machine. The specimens were pulled at a constant strain rate of until bond rupture occurred. The adhesive bond areas of the failed specimens were examined to determine the mode of failure. Results were reported as average lap shear strength in lbs/in^2.

Hydrothermal Aging Study (Wedge Test)

Wedge tests were performed by immersing wedge specimens in water at room and elevated temperatures. Stainless steel wedges were fabricated according to the dimensions specified in ASTM D3762. The tests were typically performed by inserting wedges in the open end of the specimens and driving them in with hammer blows until the ends of the wedges were flush with the ends of the specimens. The wedge specimens would then be allowed to sit at room temperature for one hour before measuring the initial crack length. The crack tip was located using a binocular microscope and its position marked with a scribe. The initial crack length was taken as the distance between the point on the wedge where the tapering begins to the crack tip. Individual sets of wedge specimens were normally placed in polyethylene containers filled with deionized water. These were covered and placed in a thermostatically controlled heating bath maintained at 25 ± 1 °C. Sets of specimens were segregated from others that had been prepared by different methods to prevent possible cross contamination during

immersion. The specimens were removed periodically to measure crack growth progression. The results of the room temperature wedge tests are provided in Appendix 2.

For the elevated temperature tests, a 10 in diameter Pyrex crystallizing dish wrapped with heating tape served as the immersion vessel. The water was thermostatted using a solid state temperature controller and an Inconel sheathed, type K thermocouple. A polyethylene cover was fitted over the top of the dish to prevent excessive evaporation. The level was maintained by periodically adding deionized water so that the specimens were continuously immersed. The water temperature was kept within $\pm 2\,^{\circ}F$ with this setup. The results of the elevated temperature wedge tests are provided in Appendix 2.

3.5 Silane Coupling Agent Hydrolysis Study

An experiment was performed to determine the relative rate of hydrolysis of 3-glycidoxypropyltrimethoxysilane (Z-6040) in water. A solution consisting of 0.074 g of dimethylformamide (DMF) (reagent grade, Aldrich), 0.200 g of 3-glycidoxypropyltrimethoxysilane (Gly-TMS) (Z-6040, Dow Corning), and 20.00 g of deionized water was prepared and stirred on a magnetic stir plate at room temperature ($25^{\circ}C$) in a stoppered 50-mL flask. The DMF was added as an internal standard for the analysis of methanol production from the Gly-TMS hydrolysis reaction. After the initial mixing, taken as time zero, the solution was sampled every ten minutes by withdrawing 1 microliter aliquots and analyzing for methanol by gas chromatography. A Hewlett-Packard 5890 gas chromatograph with FID detector was used for the analysis. A column temperature program which consisted of ramping from 50-160 $^{\circ}C$ at a rate of 20 $^{\circ}C/min$ was used in each run. From the peak ratios of methanol to DMF, which occurred at retention times of 1.68 and 3.83 respectively and a calibration curve generated from standard methanol solutions, the weight percent of methanol production over time could be calculated. A plot of room temperature Gly-TMS hydrolysis is presented in Figure 3.2 below. The results suggest that the silane is completely hydrolyzed after about 40 minutes.

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Hydrolysis of Z-6040 as a Function of Time
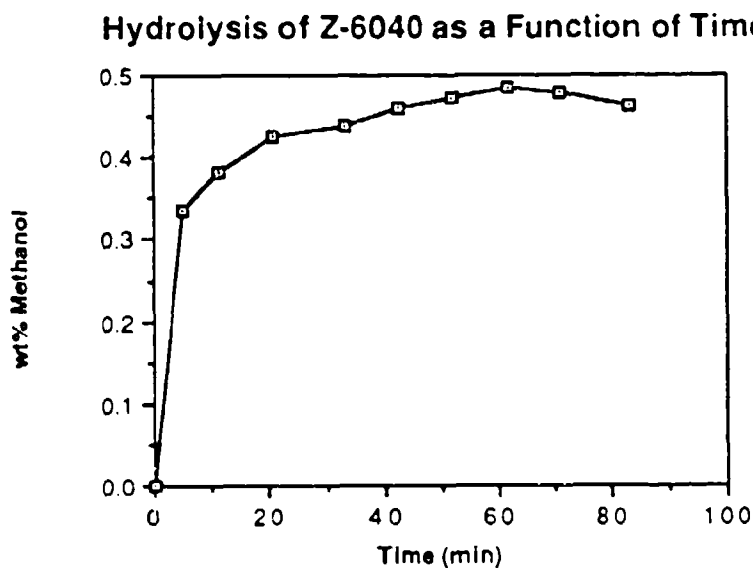
Figure 3.2. Graph of Methanol Production as a Function of Time.
From the Room Temperature Hydrolysis of
3-glycidoxypropyltrimethoxysilane in Water.

4.0 RESULTS

4.1 Characterization of Aluminum Adherends

The three basic pretreatments employed in this study were: FPL etch, alkali-silicate etch and wetsanding
with solutions of silane coupling agents and other reactive compounds. SEM was used to determine the
effects of these treatments on the adherend surface morphologies. Figure 4.1 shows an aluminum
sample after the FPL process. Viewed at low magnification (230X), the surface of a chromic acid etched
specimen appears quite rough. The striation pattern on the original aluminum specimen has been
removed by the etching. The surface oxide appears to have numerous small holes and raised areas. The
high adhesive strength and durability of FPL-etched aluminum adherends have been attributed to this
kind of micro-porous morphology.

12
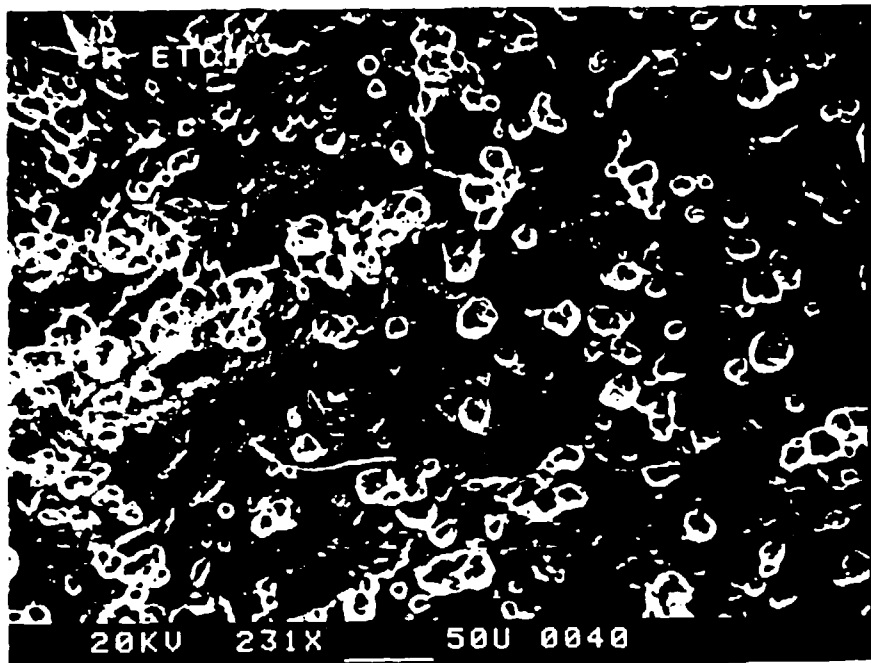
Figure 4.1 Electron Micrograph of Al 2024-T3 after FPL Etch.

Etching with alkaline sodium silicate solutions was not found to produce the same type of micro-porous surface. An electron micrograph (Fig. 4.2) of an adherend after the Sil-2 pretreatment reveals numerous holes at roughly 1000X but no evidence of the microporosity observed in chromic acid etched specimens. The silicate treatment did not appear to etch the aluminum as deeply as the FPL method. The original striation marks are clearly visible after the Sil-2 treatment.
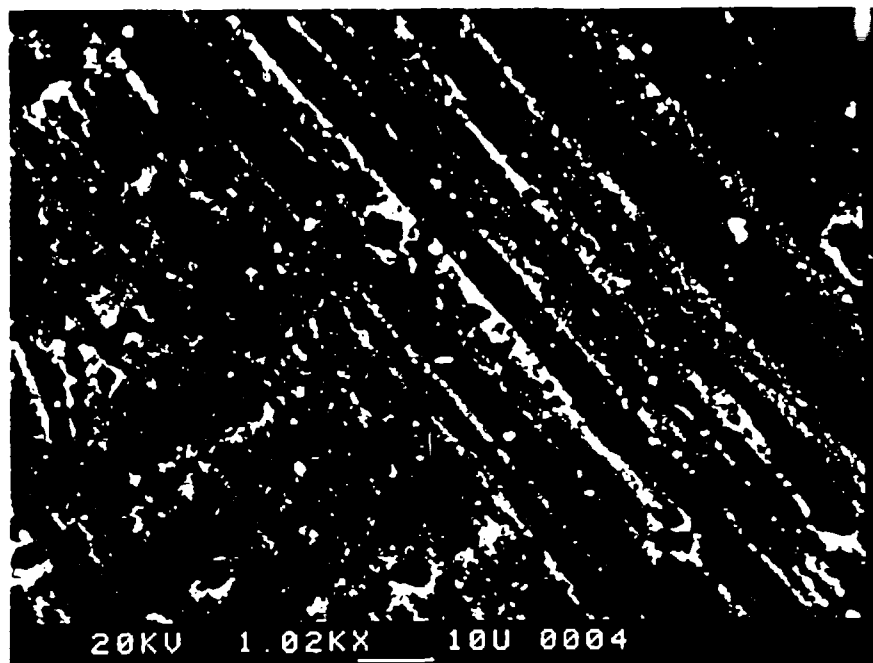
Figure 4.2   Electron Micrograph of Al 2024-T3 after Alkali-Silicate Etch

Wetsanding with hydrolyzed silane coupling agents was found to yield surfaces with deep scratches and comparatively larger surface structures than the chemical etching methods. Figure 4.3 shows an electron micrograph of an aluminum surface at approximately 1000X which had been sanded by hand with fine emery cloth and a 1% aqueous solution of Z-6040. Deep grooves and surface irregularities are evident. The large, parallel grooves running diagonally across the micrograph are presumably the original striation marks with the rest of the scratches resulting from abrasion. Apparently, the wetsanding was not sufficient to remove these surface artifacts. This may help to explain some of the inconsistencies in adhesive bond performance of samples prepared by the wetsanding process.
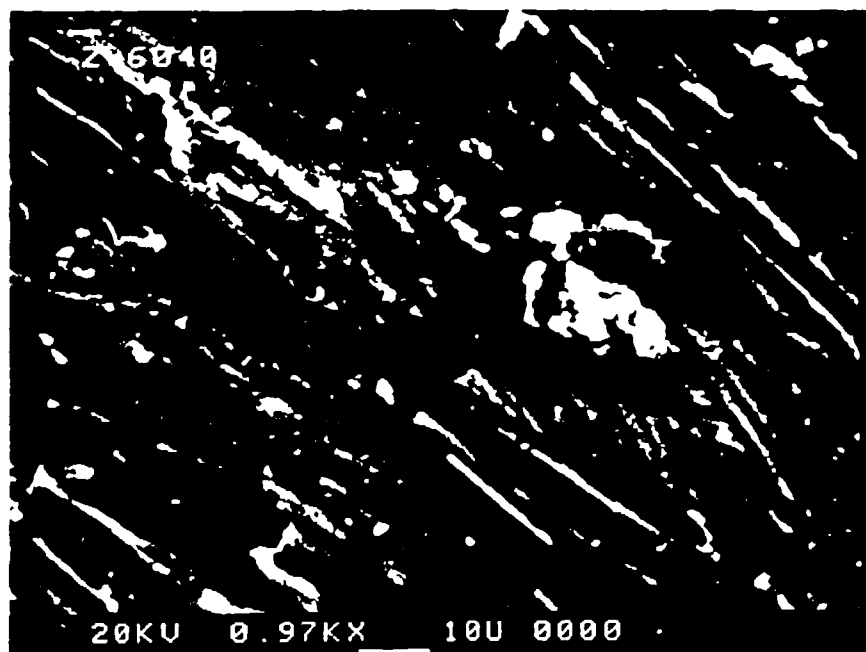
Figure 4.3   Electron Micrograph of Al 2024-T3 after Wetsanding with
Hydrolyzed Z-6040 Solution (WND-4).

The wetsanded adherend surface was also analyzed by ESCA. The analysis showed that 99.7% of the surface down to approximately 10 atomic layers was composed of carbon, oxygen and silicon. Only a trace of aluminum was detected which indicates that the wetsanding treatment leaves the adherend uniformly coated with the silane coupling agent. The ESCA spectrum is provided in Appendix 3.

4.2 Initial Adhesive Bond Strength

The results of lap shear tests on adhesive joints prepared by different methods show that initial bond strength is relatively independent of pretreatments, primers and alloys employed. The lap shear results are summarized in Table 4.1.

Table 4.1

Initial Adhesive Strength-Lap Shear Values

Sample #	Adhesive	Primer Code	Pretreatment Code	Lap Shear Strength (psi)	Standard Deviation	Mode of Failure
1	FM 123-2	BR-127	FPL	4500	100	Cohesive
14	FM 123-2	A1	Sil-1	4400	100	Cohesive
35	FM 123-2	B2	WND-4	3400	500	Mixed
35b	FM 123-2	B2	WND-4	4200	100	Cohesive
85*	FM 123-2	B2	WND-4	4500	400	Cohesive
35b2**	B1	B2	WND-4	600	200	Mixed

* Al 7075-T6 adherend
** Average of four samples

The only instances where partial adhesive failure occurred was observed with samples 35 and 35b2. The difference between the preparation of samples 35 and 35b was that the primer in 35 was cured at $65^{\circ}C$ for one hour while the primer in 35b was cured at room temperature for one hour. Sample 35b failed cohesively in the adhesive and sample 35 failed in a mixed adhesive-cohesive mode. FTIR analysis of both failed lap shear adherends revealed primer material on both surfaces. A comparison of the two IR spectra showing the region of siloxane absorbance is provided in Appendix 1. Apparently, the failure in sample 35 occurred cohesively in the primer. When the same primer was applied and cured at room temperature (# 35b), the tensile shear strength was comparable to FPL-etched specimens.

It is postulated that this difference in initial adhesive strength may be attributed to the rapid epoxy cure rate at elevated temperatures. If the primer is fully cured before coming in contact with the adhesive, there may not be enough free epoxy or amine groups in the primer to covalently bond with the epoxy-based adhesive. Also, the rate of epoxy crosslinking at higher temperatures may be much faster than the siloxane incorporation resulting in gross phase separation of the two components. Silicone material was found on both the primer and adhesive sides of the failed specimens. The elimination of a weak, silicone-rich interlayer may also help explain the improved durability of sample 35b in the wedge test.

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An attempt was made to use one of the primer formulations as an adhesive. Primer B1 was coated onto a 0.01"-thick polypropylene scrim cloth, allowed to dry at room temperature for 24 hours, and the resulting supported adhesive used to bond pretreated Al 2024-T3 adherends. The specimens failed primarily by an adhesive mechanism with some of the failure resulting from the support pulling away. The low lap shear strength of these specimens could be partially attributed to the same primer-adhesive interfacial problems described for sample 35. In this case the adhesive may have been too fully cured and thus unreactive toward the primed surface.

4.3 Adhesive Bond Durability

The durability of adhesive bonds to aluminum aircraft alloys in a humid environment was determined for a number of pretreated and primed adherends by the modified wedge opening test. The crack extension as a function of time was measured for wedge specimens immersed in water at $70\,^{O}F$, $120\,^{O}F$, and $140\,^{O}F$. The results of these analyses are tabulated in Appendix 2. Failure analyses were performed for each set by breaking the specimens apart and examining the debonded area by FTIR, SEM and in some cases ESCA.

The Effects of Pretreatments on Bond Durability

Adherend pretreatments were found to significantly affect the hydrothermal stability of adhesive bonds on aluminum. The room temperature wedge test results for seven sets of specimens that were prepared by different pretreatments are provided in Figure 4.4.

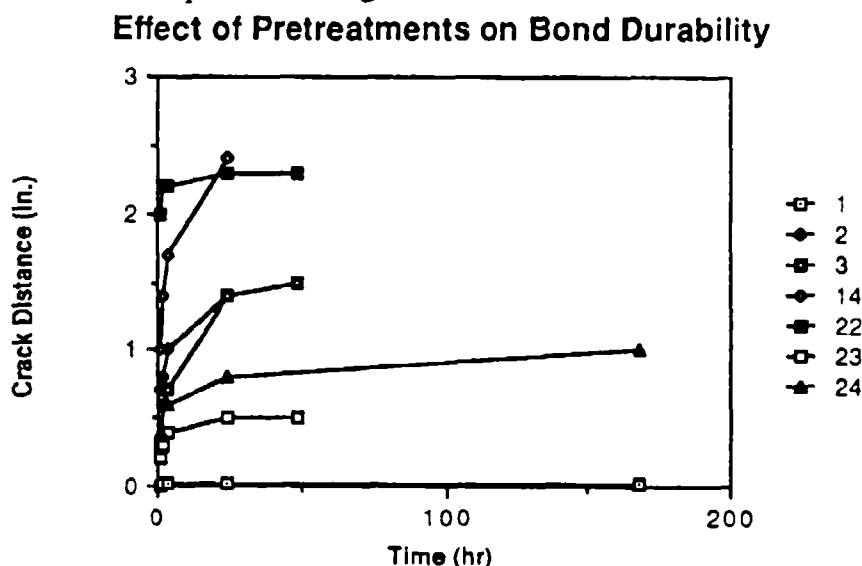**Effect of Pretreatments on Bond Durability**

Figure 4.4.   Results of Room Temperature Wedge Tests Suggesting
that Pretreatments Play a Significant Role in Bond Durability.

The wedge test results indicate that the FPL etch control treatment (sample 1) indeed produces durable adhesive bonds while etching with alkali-silicate solutions (samples 14 and 22), wetsanding with primer solutions in organic solvents (samples 2 and 3), and wetsanding with Z-6040 in tetrahydrofuran (sample 24) do not appear to yield stable bonds. An SEM photomicrograph taken at 1000X of the debonded region of a failed sample 14 specimen (Figure 4.5) shows the macroporous surface left by the alkali-silicate etching. The white colored region at the left is the adhesive.
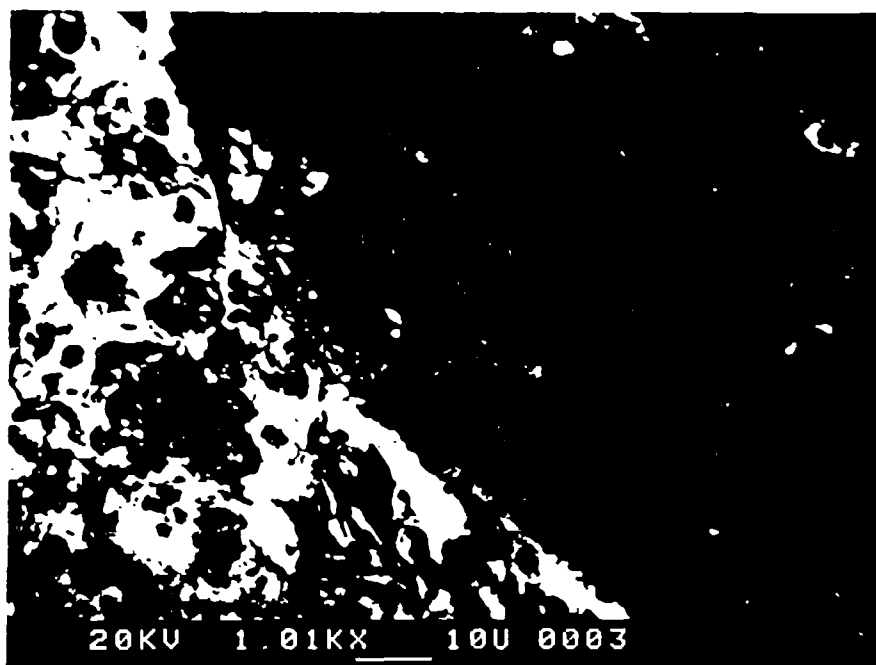
Figure 4.5   Electron Photomicrograph of Sample 14 Adherend After Room Temperature Wedge Test

Wetsanding with aqueous hydrolyzed Z-6040 solutions however, appears to promote a degree of adhesive bond stability to hydrothermal stress. Sample 23 outperformed the other experimental pretreatment methods in this set but was clearly not as effective as the control FPL surface treatment.

The FPL and wetsanding pretreatment methods were also found to be superior to the others in terms of initial bond strength. A plot of the initial crack distances (A_o) which is an indirect measure of adhesive bond strength for these samples is given in Figure 4.6. Samples 1 and 23 have lowest A_o values in this series.

Effect of Pretreatments on Initial Crack Distance
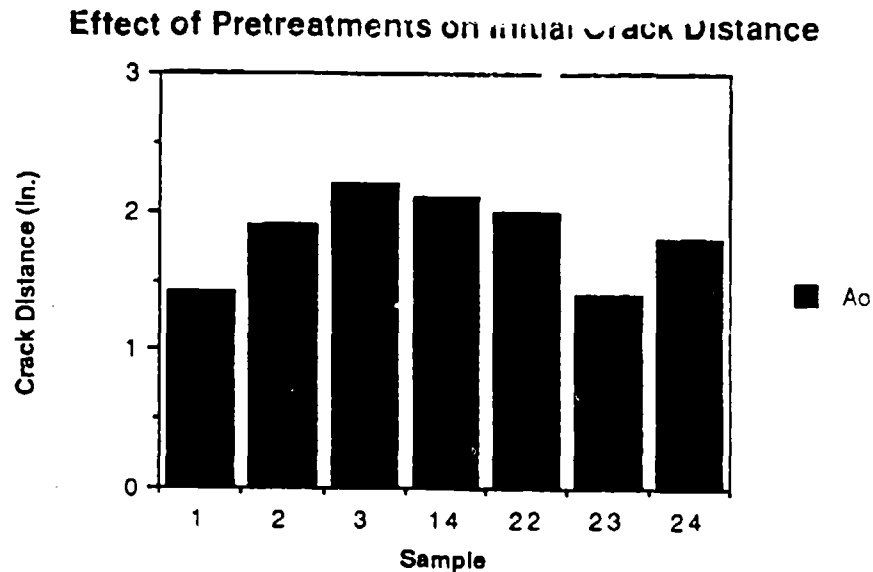
Figure 4.6   Bar Graph Showing the Effects of Different Pretreatments on A_0.

The Effects of Primer Structure on Bond Durability

Having determined that the WND-4 pretreatment showed the most promise among the experimental surface treatments employed, the effects of primer structure were investigated. Eight primers were applied to Al 2024 adherends which had been prepared by the WND-4 method. Wedge specimens were fabricated using FM 123-2 adhesive and tested by room temperature immersion. The results of these wedge tests are presented in Figures 4.7 and 4.8.

Effect of Primer Type on Bond Durability
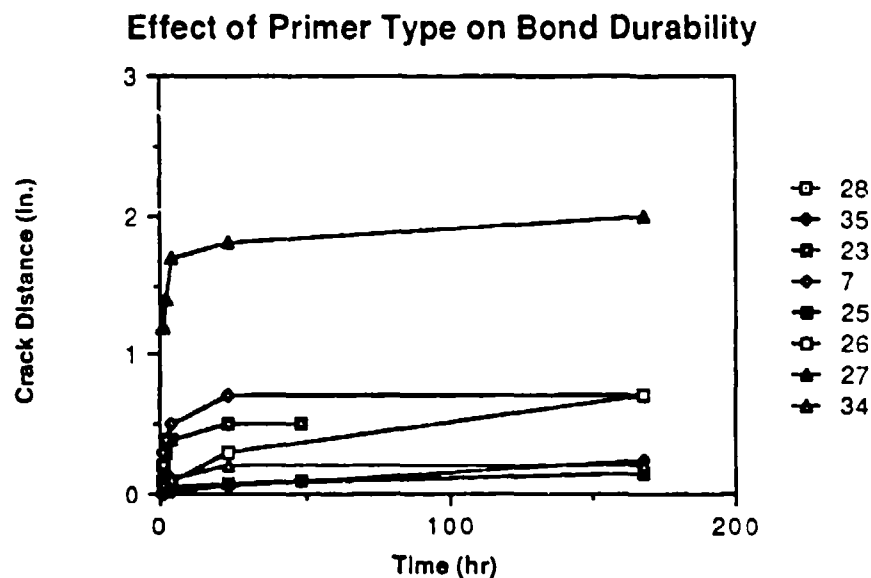
Figure 4.7   Results of Room Temperature Wedge Test for Samples Prepared from Different Primers.

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Effect of Primer Type on Initial Crack Distance
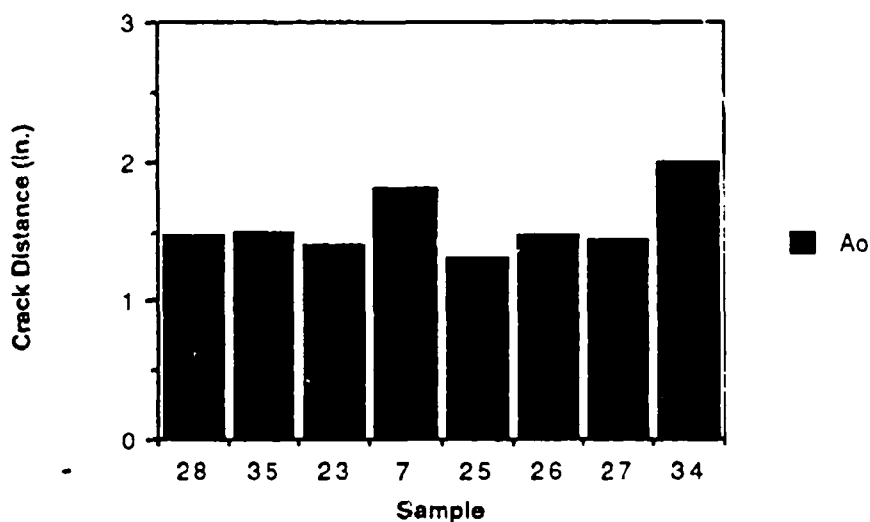
Figure 4.8   Bar Graph Showing the Effects of Different
              Primers on A_0

Four samples (28, 35, 25, and 34) appeared to significantly outperform the others in terms of durability while the comparative A_0 data was inconclusive. Two of the samples which displayed greater water sensitivity (27 and 23) were prepared from primers based on a cycloaliphatic amine curing agent. Primers formulated with an aromatic amine curing agent were used on the samples which were found to be more durable. An aromatic amine crosslinker was also used in the primer for sample 7 which showed some water sensitivity. This primer also contained a fairly high molecular weight polysiloxane additive which may have not effectively incorporated into the crosslinked copolymer. An SEM photomicrograph taken at approximately 1000X of the debonded area of a failed sample 7 wedge specimen is shown in Figure 4.9. Deep striation and abrasion marks are evident on the surface as well as the absence of organic material which in SEM would tend to blur the image.
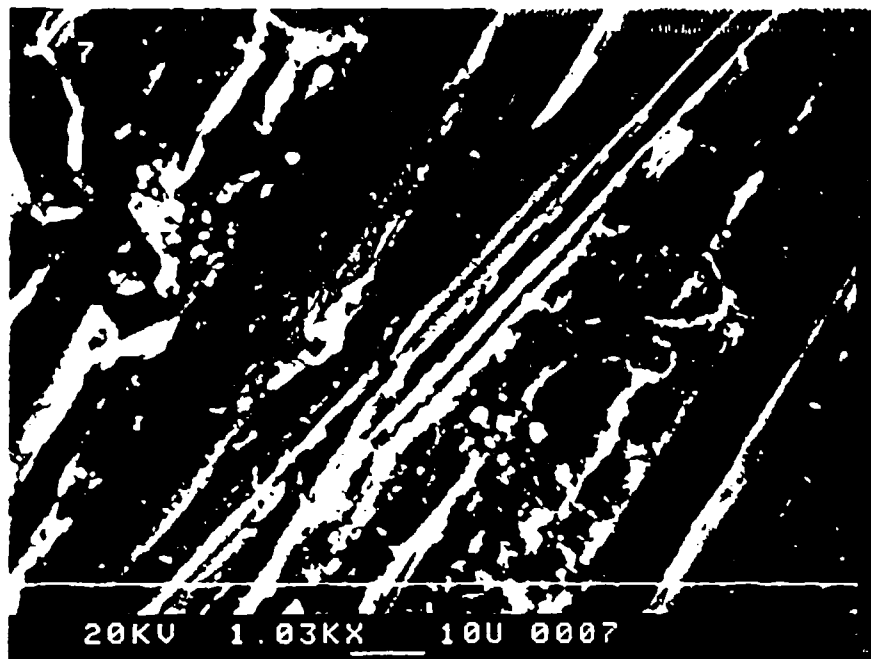
Figure 4.9.   Electron Photomicrograph of Sample 7 Adherend After
Room Temperature Wedge Test.

Sample 26, which was primed with a 25 % solution of X1-6100 aromatic silane coupling agent in isopropanol did not perform as well as some of the other primers tested but the SEM analysis of a failed adherend showed an interesting surface (Figure 4.10). The photomicrograph, taken at approximately 1000X is somewhat out of focus due to the presence of organic material on the surface. This blurriness is in marked contrast to the sharp image shown in Figure 4.9 for sample 7.
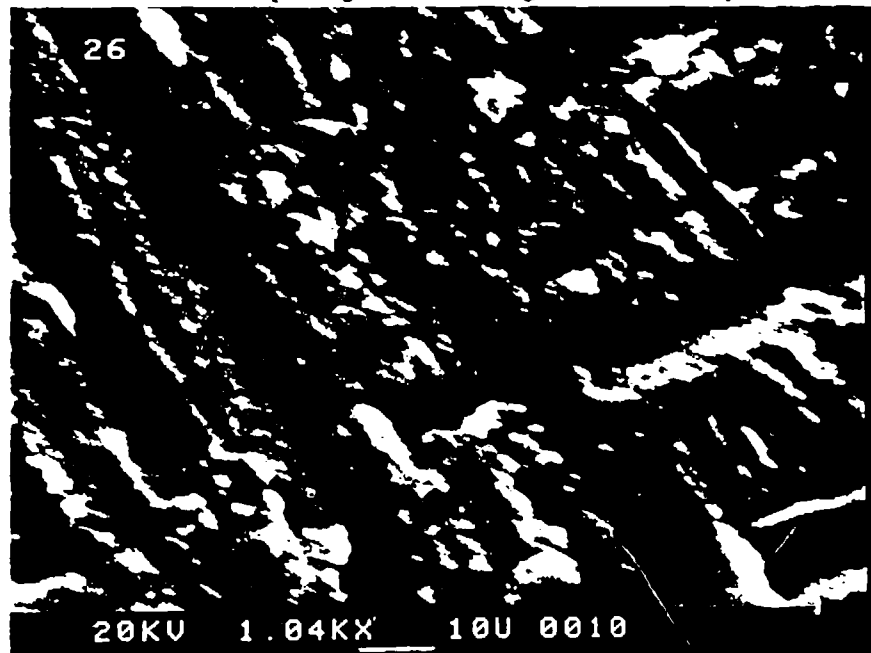
Figure 4.10.   Electron Photomicrograph of Sample 26 Adherend
After Room Temperature Wedge Test.

The wedge test results for the four samples which had performed the best in this series are shown in Figure 4.11. Besides having aromatic amine-based primers in common, these samples were all prepared with primers containing short-chain polysiloxanes or no polysiloxane additives. The inclusion of phenyl-substituted polysiloxane (sample 28) appeared to be beneficial as did the absence of silicone resin (sample 34). It should be noted that two out of the five specimens in the sample 34 set had crack extensions below 0.1inch/week at room temperature. The fact that these two specimens were significantly more hydrothermally stable than the others suggests that the pretreatment may not have been uniform.

Effect of Primer Type on Bond Durability
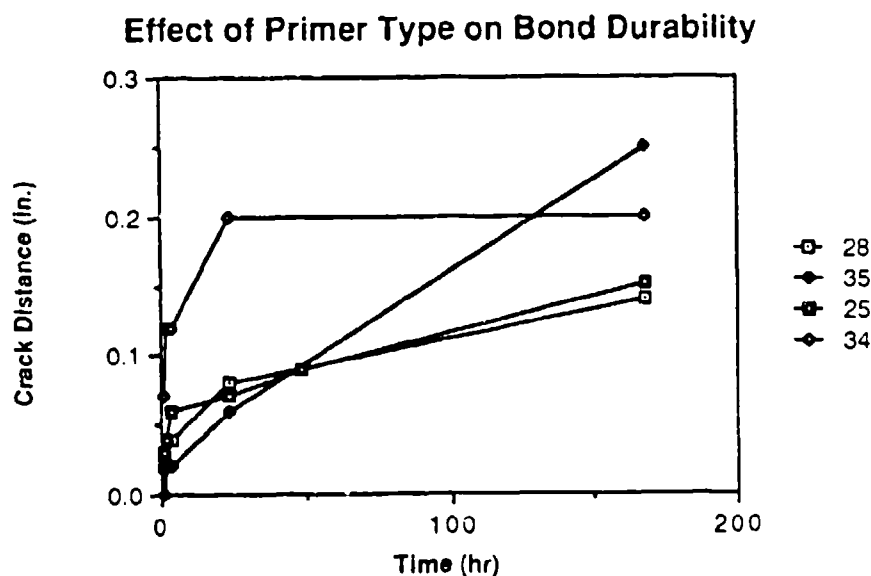
Figure 4.11.   Room Temperature Wedge Test Results for Selected
Samples Prepared by the Same Pretreatment Method

Samples 35 and 25 were prepared using similar primer formulations which differed only in the ratio of polysiloxane to GAPTES. Both performed very well over the first 50 hours of the wedge test. Figure 4.12 shows an SEM photomicrograph of a failed sample 35 adherend focussing the interfacial debonded region. There appears to be a very jagged interface between the adherend and the adhesive suggesting a strong interaction between the primer and adherend. The debonded area shows very little organic material remaining on the surface.

21
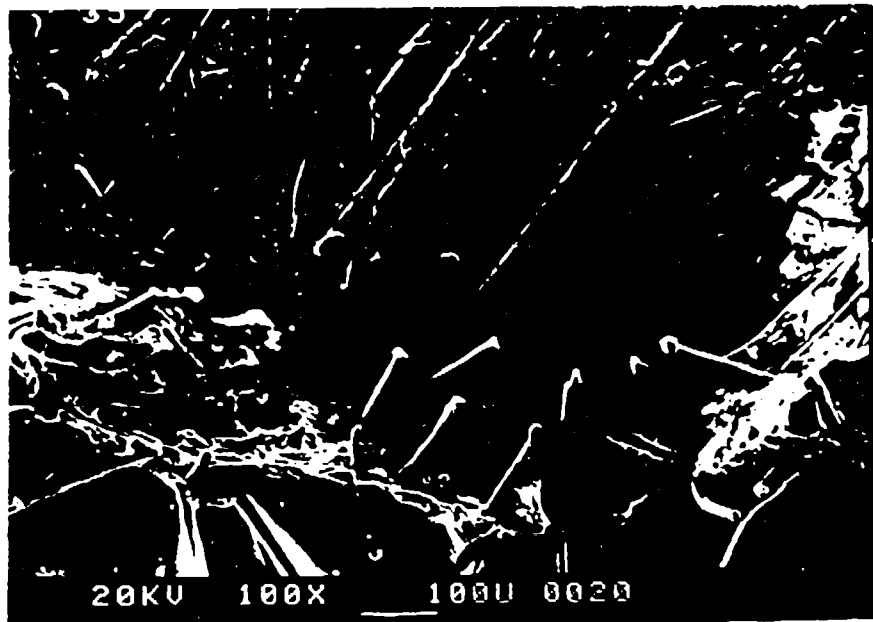
Figure 4.12.   Electron Photomicrograph of Sample 35 Adherend
                      After Room Temperature Wedge Test.

The Effects of Primer Cure Temperature on Adhesive Bond Durability

The differences observed in the initial lap shear strengths of samples prepared with the same primers but different primer cure schedules led to an investigation of this effect on adhesive bond durability. Figure 4.13 shows the results of two groups of samples where in each group, one set had primers cured at room temperature for one hour before bonding (samples 7 and 35) and the other had primers cured at $65^{\circ}C$ for one hour before bonding (samples 7b and 35b). Clearly, the specimens whose primers were cured at room temperature produced bonds with superior hydrothermal stability.

Effect of Primer Cure on Bond Durability
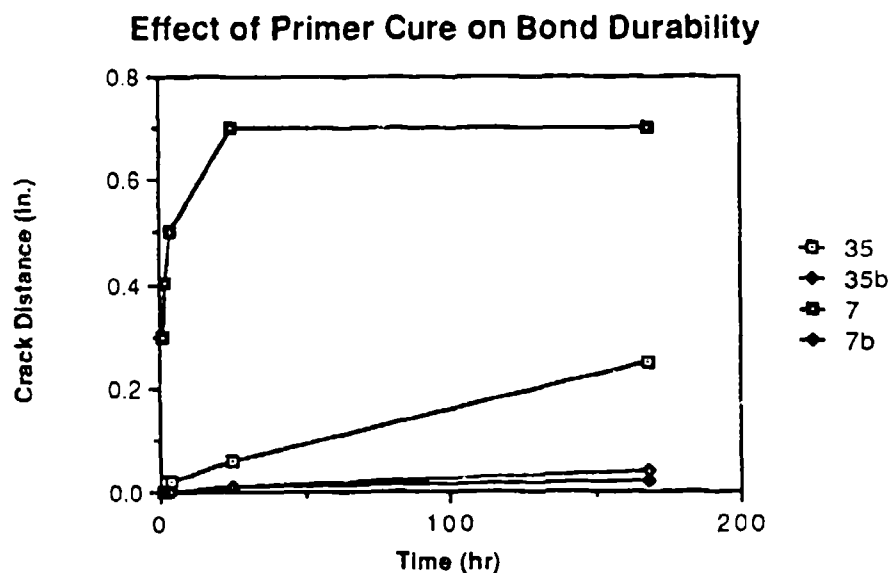
Figure 4.13.   Room Temperature Wedge Test Results Suggesting that
                      Curing Primers at Room Temperature Improves Bond Durability.

The more dramatic difference in performance between samples 7 and 7b may stem from the notion of phase separation during primer cure. This primer is based on a fairly high molecular weight polysiloxane which may not have a chance to fully incorporate into the epoxy matrix when the reaction is carried out at elevated temperature. The effect of primer cure temperature on initial crack length, A_0 was not found to be significant. A graph of this relationship is given in Figure 4.14.

Effect of Primer Cure on Initial Crack Distance
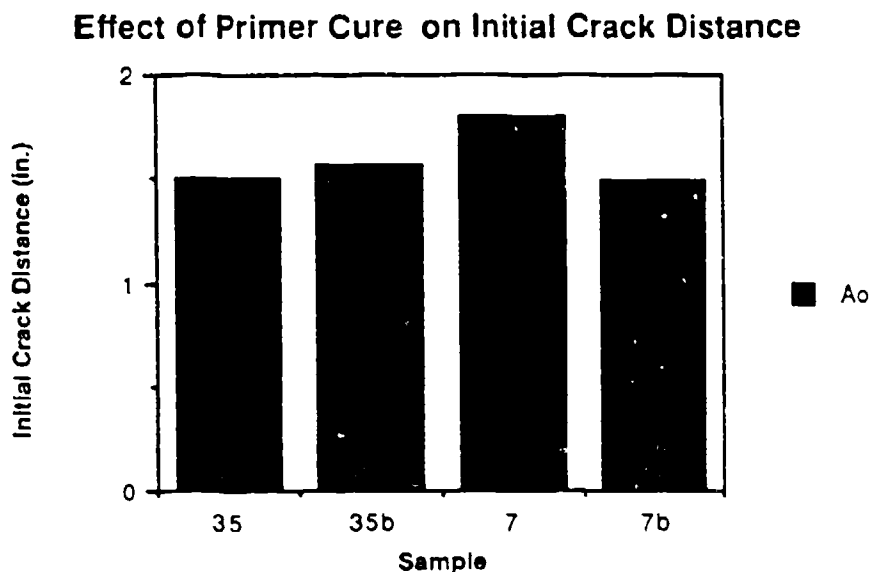
Figure 4.14   Bar Graph Showing the Effects of Primer Cure
                     Temperature on A_0.

Primer Silicone Content and Its Effect on Bond Durability

A series of wedge specimens was prepared from primers formulated with varying loadings of the same polysiloxane resin (D7PDMS). The alloy, pretreatment, primer cure conditions and adhesive were all held constant. The results of the wedge tests are shown graphically in Figure 4.15. Basically, the data suggest that a 5 % loading of polysiloxane gives optimal durability. Above this level, the hydrothermal stability appears to rapidly fall off. This may be attributed to the greater degree of phase separation in copolymers with higher polysiloxane contents.

23

Effect of Silicone Content on Bond Durability
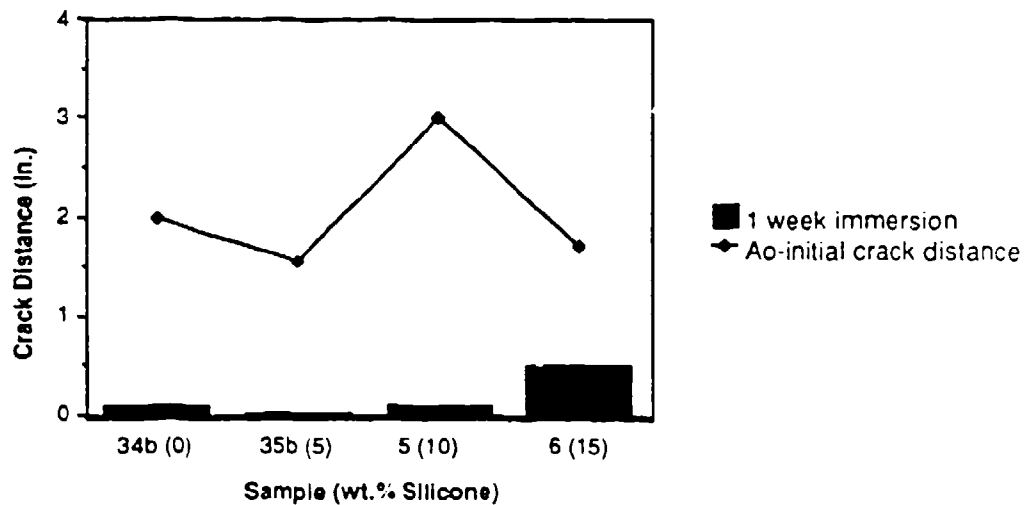
Figure 4.15.   Room Temperature Wedge Test Results for Samples
Prepared from Primers with Varying Silicone Contents.

The Effects of Silicone Block Length on Adhesive Bond Durability

The effect of varying the size of the silicone blocks within the experimental primer resins while holding the total silicone content at 5 % is highlighted in Figure 4.16. The data suggest that the durability of the adhesive bonds is relatively insensitive to the type of silicone additive used in the primer provided the total silicone content is below a certain level. The initial crack length, A_0, was also found to be insensitive to the size of the polysiloxane blocks used in the primer resins.

Effect of Silicone Block Length on Bond Durability
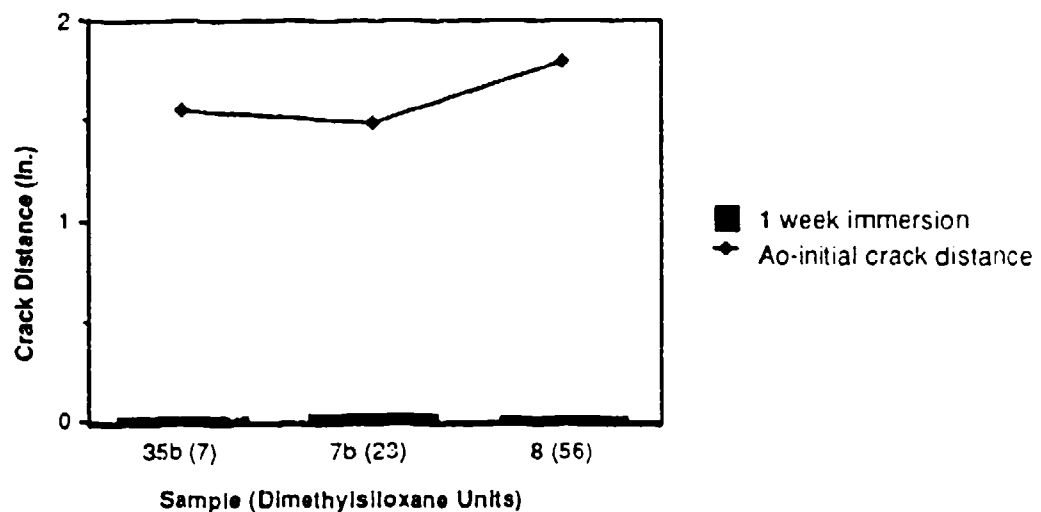
Figure 4.16.   Room Temperature Wedge Test Results for Samples
Prepared from Primers with Varying Silicone Block
Lengths.

An interesting surface effect was observed upon SEM analysis of a failed sample 8 adherend. This sample had been prepared with a primer based on a high molecular weight polysiloxane resin (D₇PDMS). A photomicrograph of the debonded region taken at approximately 500X is shown in Figure 4.17. Apparently an organic layer was left on the debonded surface. In the majority of the samples examined, the debonded regions were devoid of organic material.
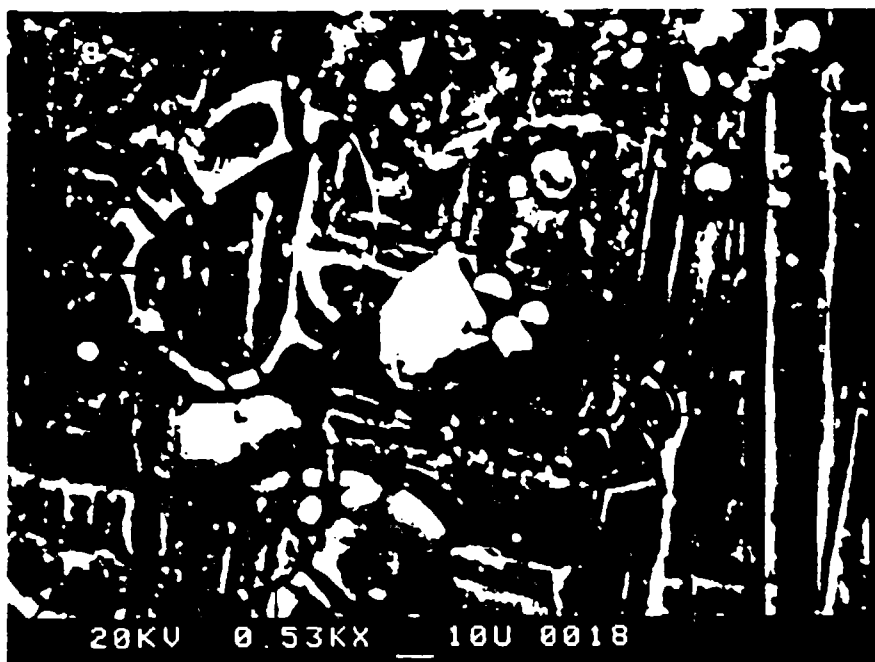
Figure 4.17   Electron Photomicrograph of Sample 8 Adherend
                   After Room Temperature Wedge Test

Adhesive Bond Durability on Different Aluminum Alloys

The majority of the experimental primer evaluations performed in this program involved adhesion to alloy 2024-T3. Lap shear studies showed that the initial adhesive strength of bonds prepared by the WND-4 wetsanding pretreatment and an experimental epoxy-silicone primer was the same for Al 2024-T3 and Al 7075-T6 adherends. Wedge tests, however showed that the durability of adhesive bonds on Al 7075 alloy was more sensitive to the pretreatment method employed. Figure 4.18 shows the results of room temperature wedge tests for adhesive specimens prepared by two different pretreatments and primers on Al 7075-T6.

25
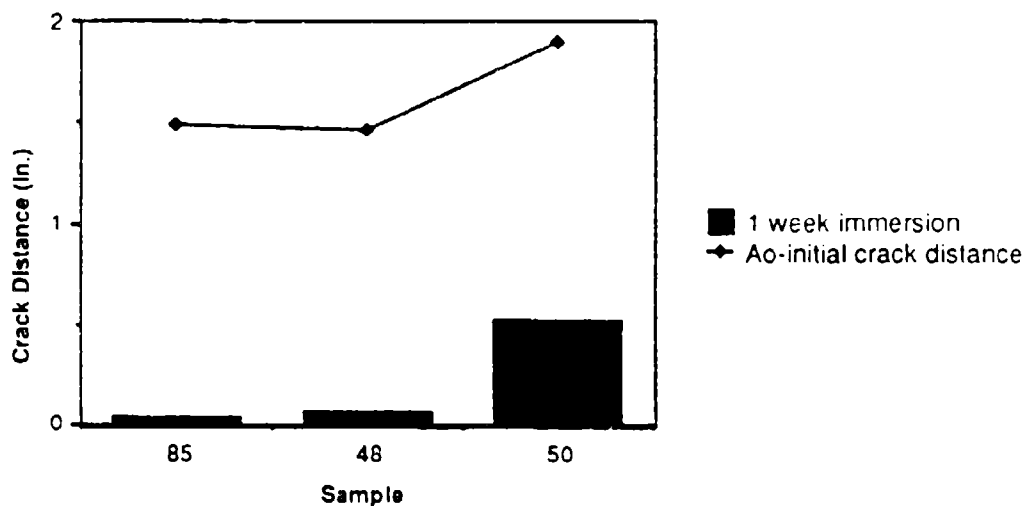
Figure 4.18   Room Temperature Wedge Test Results for Samples
Prepared from Al-7075-T6 Adherends.

The FPL pretreatment was used to prepare samples 85 and 48. Sample 85 was primed with experimental primer B2 while the commercial primer, BR-127 was used on sample 48. Both sample sets performed well in the wedge test implying that the adhesive bond durability was relatively insensitive to the primer used and dependent on the adherend pretreatment. Sample 50, which had been prepared by the WND-4 pretreatment method and primed with experimental formulation B2 was found to exhibit greater bond sensitivity to hydrothermal stress. A photomicrograph of a failed sample 50 adherend taken at approximately 1000X and focussing on the debonded region is provided in Figure 4.19.
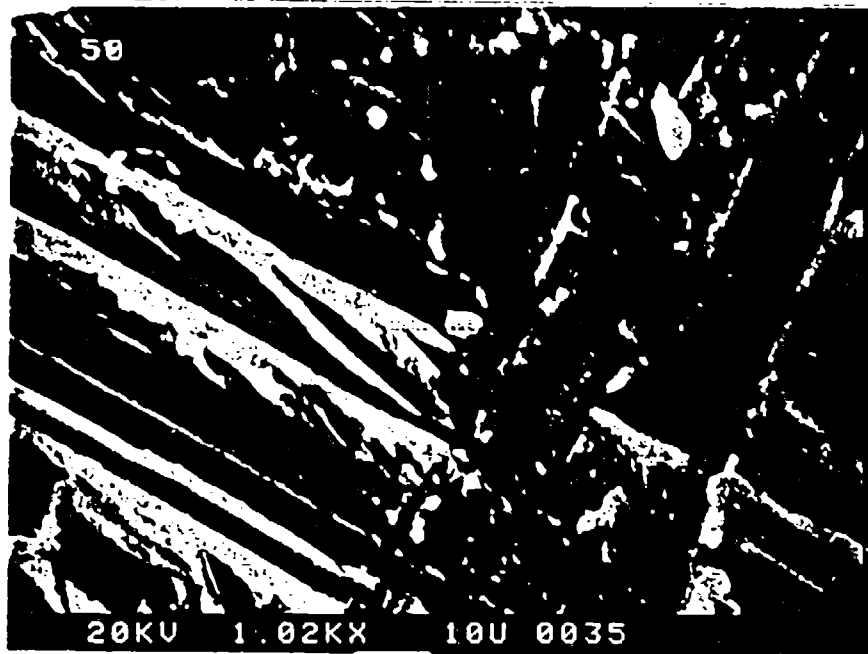
Figure 4.19   Electron Photomicrograph of Sample 50 Adherend
After Room Temperature Wedge Test.

The debonded area appears to be free of organic material which implies that the mode of failure was adhesive between the primer or pre-primer and the aluminum substrate. The striation marks on the metal surface are also quite visible in the picture. This suggests that the wetsanding treatment did not deeply abrade the surface. One possible reason for the experimental surface preparation's reduced performance on this alloy is the hardness of the metal. A typical 7075 series alloy has a hardness of 150 BHN as opposed to 120 BHN for alloy 2024-T3[6]. Harder alloys may be more difficult to uniformly abrade by hand.

The deep grooves observed in the SEM micrographs of 7075 adherends may also trap water or other contaminants between the metal and primer layers. What may be needed is a high pressure abrasion technique to effectively remove these surface imperfections and provide more intimate contact between the hydrolyzed silane pre-primers and freshly formed aluminum. Reproducibility of the pre-bond surfaces is believed critical for long-term adhesion durability. An example of the reproducibility of adhesive samples prepared by the FPL pretreatment and different primers on Al 2024-T3 and Al 7075-T6 substrates is shown in Figure 4.20.

Effect of Substrate on Bond Durability

■ 1 week immersion
◆ Ao-initial crack distance
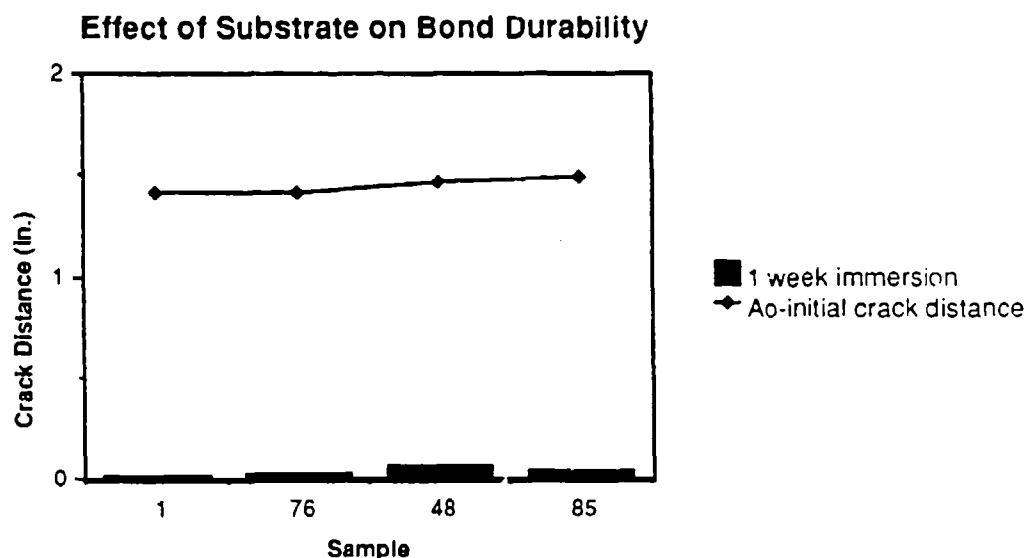
Figure 4.20.   Room Temperature Wedge Test Results for Samples
Prepared from Al 7075-T6 and Al 2024-T3 Adherends
Suggesting the Dependence of Bond Durability on
Surface Pretreatment.

All of the wedge test specimens in this study showed some signs of metal corrosion after a week of continuous water immersion. The degree of corrosion observed in the sample 76 set, however, was far greater than the rest. This sample was prepared on Al-2024 by the FPL method followed by priming with experimental primer B2. Apparently the chromic acid etch yields a surface oxide layer that is more susceptible to corrosion than non-etched aluminum surfaces. The performance of the adhesive bond under these conditions suggests that the silicone-based primer prevented the corrosion from entering the bond line. A photograph of one of these wedge samples is shown in Figure 4.21.
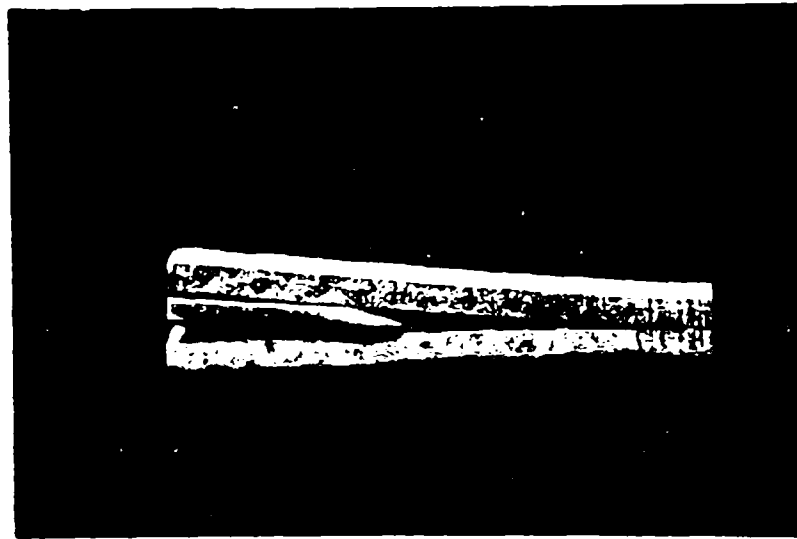
Figure 4.21.   Sample 76 Wedge Test Specimen After One Week of
                    Room Temperature Water Immersion.

Accelerated Hydrothermal Aging Study

Adhesively bonded joints used in the manufacture and repair of aluminum aircraft structures in the field must perform effectively over a wide temperature and humidity range. Accelerated hydrothermal aging studies consisting of elevated temperature wedge immersion tests were conducted on two sets of adhesive samples. One set was prepared by the WND-4 pretreatment method and B2 experimental primer on Al 2024-T3 (sample 40) and the other by the FPL method and BR-127 primer on 2024-T3 (sample 42). The wedge specimens were continuously immersed for one week at 120 ^{O}F and one week at 140 ^{O}F. The results of this accelerated aging study are presented graphically in Figure 4.22.

Thermal Stability of Adhesive Bonds
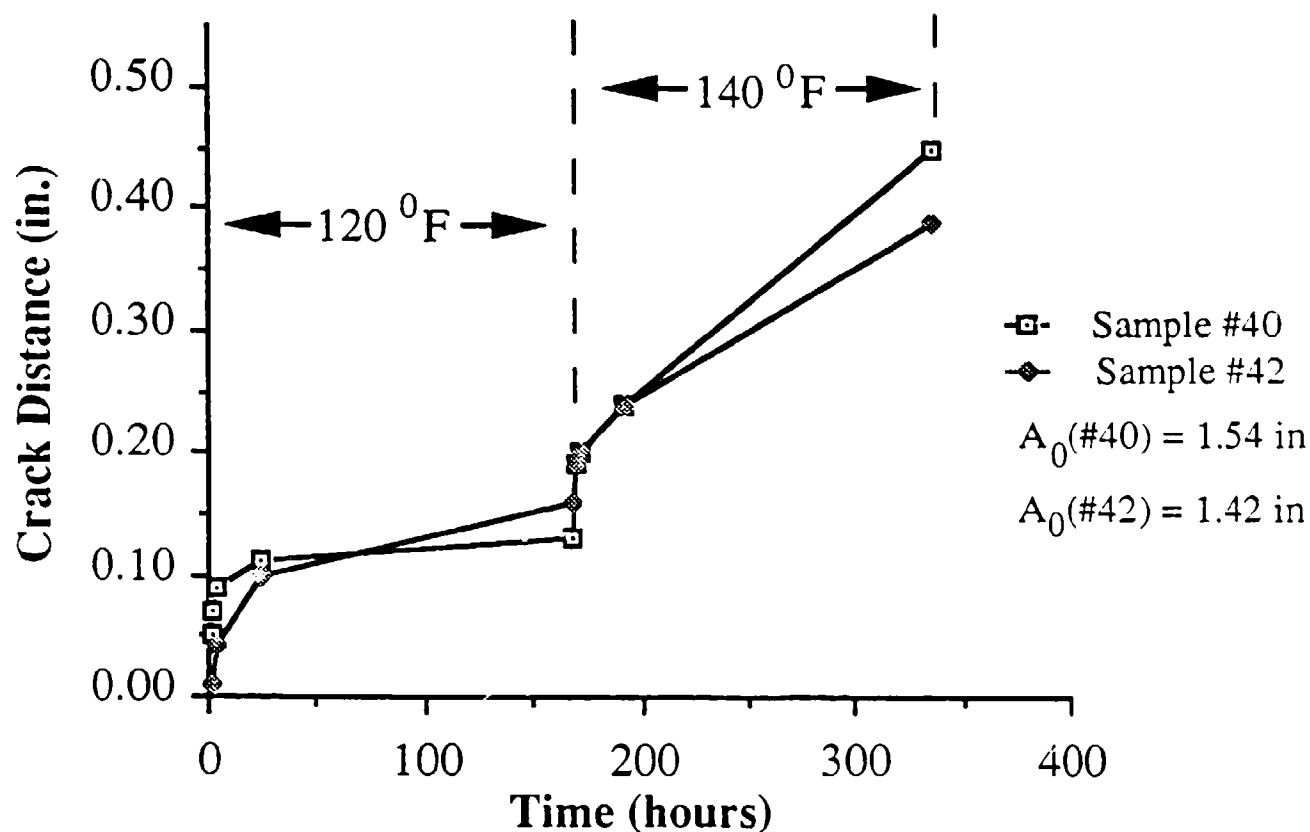
Figure 4.22.   Results of Accelerated Aging Study for Samples 40 and 42.

The two sets of adhesive specimens showed comparable hydrothermal stability under these extreme conditions. SEM and ESCA were used to probe the debonded regions of the failed specimens. Two SEM photomicrographs taken at approximately 240X and 1000X of failed sample 40 adherends in the debonded regions are shown in Figures 4.23 and 4.24 respectively.
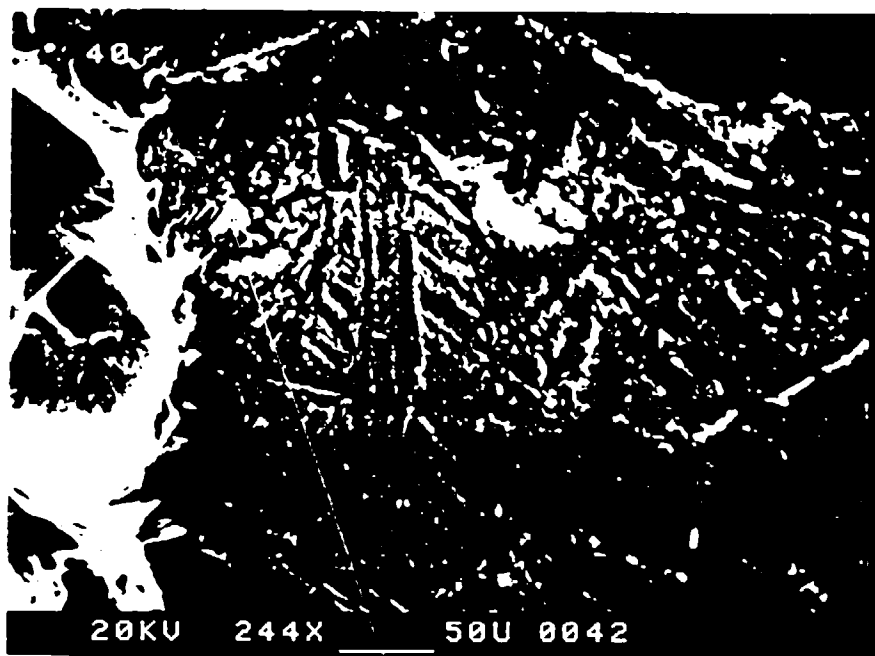
Figure 4.23.   Electron Photomicrograph of Sample 40 Adherend After Room Temperature Wedge Test, Highlighting the Adhesive-Debonded Region Interface.

Figure 4.24.   Electron Photomicrograph of Sample 40 Adherend After Room Temperature Wedge Test Showing Debonded Region.

The interface between the bonded adhesive and debonded area appears jagged in Figure 4.23 which suggests that much force was needed to break the bond. The close-up of the debonded region, shown in Figure 4.24 is blurred which indicates that an organic layer remained on the surface after bond failure. ESCA analysis of this region revealed that the surface was composed of roughly 30 % carbon but failed to detect any silicon. This suggests that the failure may have occurred either cohesively between primer and adhesive, within the adhesive itself or between the preprimer (Z-6040) and primer (B2). The silicone-rich material may have been left on the other adherend or covered by other organic material. The ESCA spectra are included in Appendix 3.

SEM analysis of the failed sample 42 surfaces suggest a different type of failure. Photomicrographs taken at approximately 150X and 400X of failed sample 42 adherends in the debonded regions are shown in Figures 4.25 and 4.26, respectively.
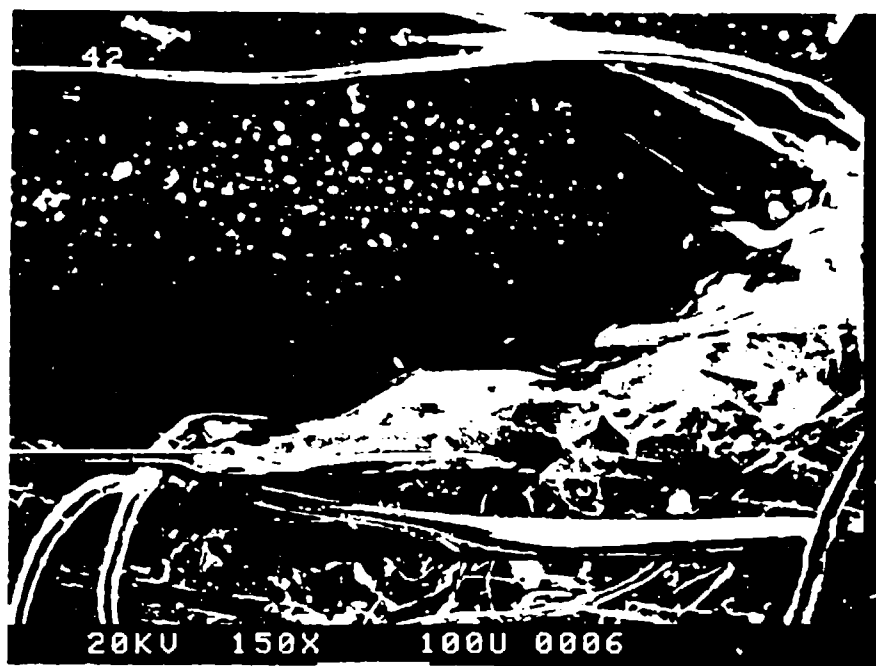
Figure 4.25.   Electron Photomicrograph of Sample 42 Adherend
                    After Room Temperature Wedge Test, Highlighting the
                    Adhesive-Debonded Region Interface.

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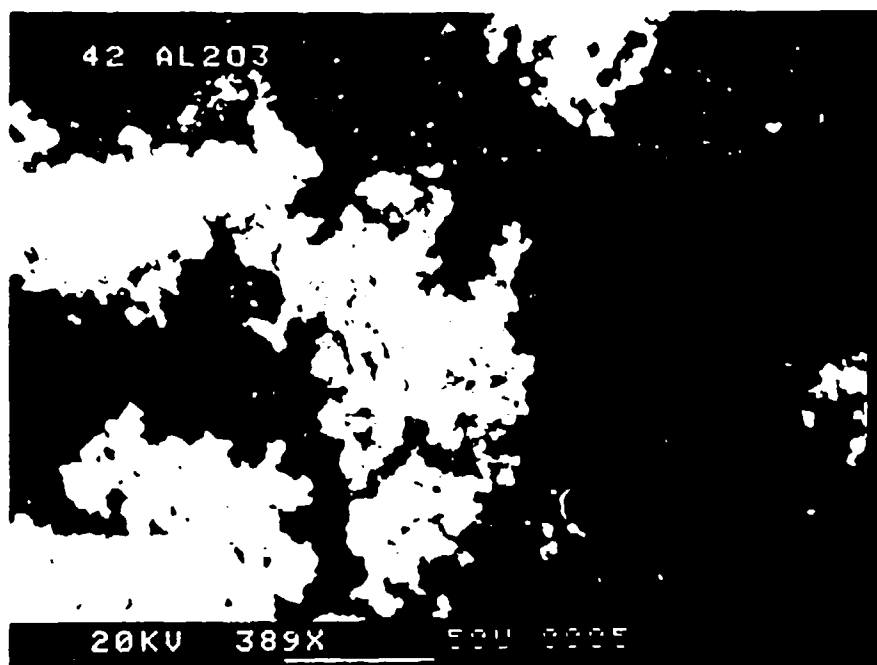
Figure 4.26.   Electron Photomicrograph of Sample 42 Adherend
                      After Room Temperature Wedge Test Showing Debonded
                      Region.
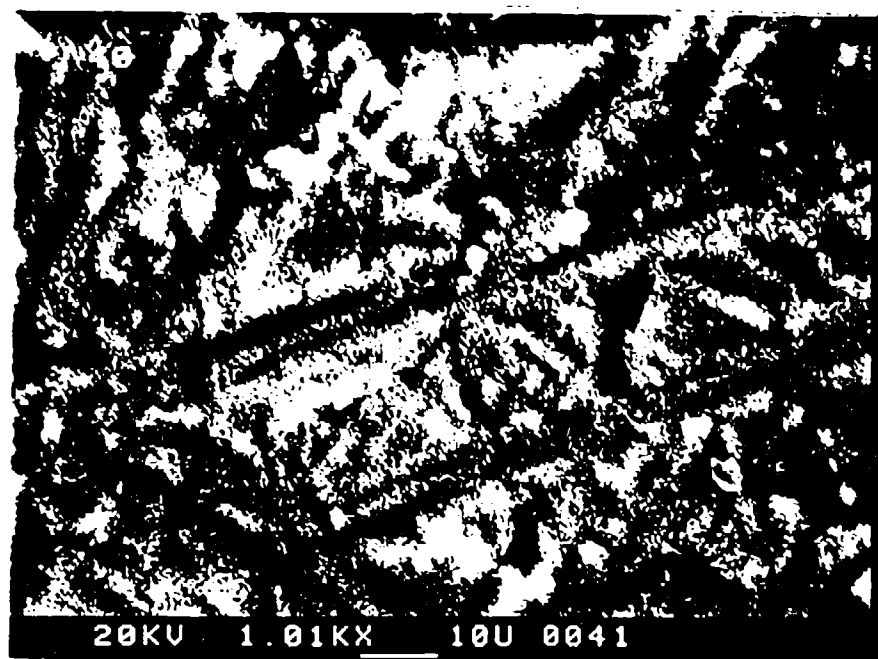
In Figure 4.25, the interface between bonded adhesive and the debonded region of a failed sample 42
adherend is highlighted. A number of round white structures were observed in the debonded area.
These were identified as aluminum oxide upon closer examination. The debonded surface was also
probed by ESCA and found to have only a trace of carbon present. This suggests that the mode of
adhesive failure was adhesive between the primer and adherend. The formation of macroscopic
aluminum oxide structures in the debonded regions is reminiscent of the corrosion observed on the
outside of the 76 sample wedge specimens after immersion (Figure 4.21). The ESCA spectra are
included in Appendix 3.

5.0 DISCUSSION

The results of this study emphasize the importance of surface treatment and primer structure on the
durability of adhesively bonded aluminum structures. A series of primer formulations based on
phosphate-modified, epoxy-silicone copolymers was found to produce adhesive bonds of exceptional
strength and durability when applied over suitably pretreated aluminum adherends. The modified
Windecker wetsanding method (WND-4) was found to be particularly effective on softer aluminum
alloys such as Al 2024 when used in combination with these experimental primers. The primers also

produced bonds of outstanding durability on either Al-2024-T3 or Al-7075-T6 when preceded by an FPL treatment. This latter result suggests that the condition of the substrate surface before priming is a critical variable in the bonding process.

Wetsanding by hand generally was found to give acceptable results for the small specimens used in testing adhesive properties, though the uneven surfaces produced by this method may have contributed to some of the inconsistencies observed in the durability experiments. For example, two out of the five wedge specimens in the sample 34 set which had been wetsanded (WND-4) before priming outperformed the others in terms of durability by over 100 %. The high relative uncertainties observed in the average wedge test results for samples 26, 15b, and 29 as well as the differences in performance between alloys 2024 and 7075 may be attributed to non-uniformity in the pre-prime abrasion process. SEM analyses of the adherends before and after adhesion testing show that wetsanding by hand produces surfaces with only macroscopic roughness and does not effectively remove the striation marks on the metal. The FPL etching process was found to yield much more uniform surfaces with microporous morphologies.

In order to demonstrate that more uniform adherend surfaces could be obtained without the use of corrosive chemical or electrical etching, two aluminum alloy samples were mechanically abraded by a high pressure grit blasting method. The vapor honing of the aluminum surfaces was performed with a 10,000 psi grit blasting unit courtesy of Advanced Water Blast, Inc. of Decatur, Georgia. The 6" X 6" X 0.125" plates were abraded with high pressure water slurries of a fine, garnet-type abrasive media. The 2024-T3 sample was honed for a total of 15 seconds at 5,000 psi and the 7075-T6 plate was honed for a total of 30 seconds at a pressure of 3,000 psi. A cross-spray technique analogous to paint spraying was employed with the hand held wand. This water blast method produced very uniformly abraded surfaces on both adherends.

The following photomicrographs (Figures 5.1, 5.2, 5.3, 5.4, and 5.5), taken at 25X show the effects of the different pretreatments on typical aluminum aircraft alloys.

33
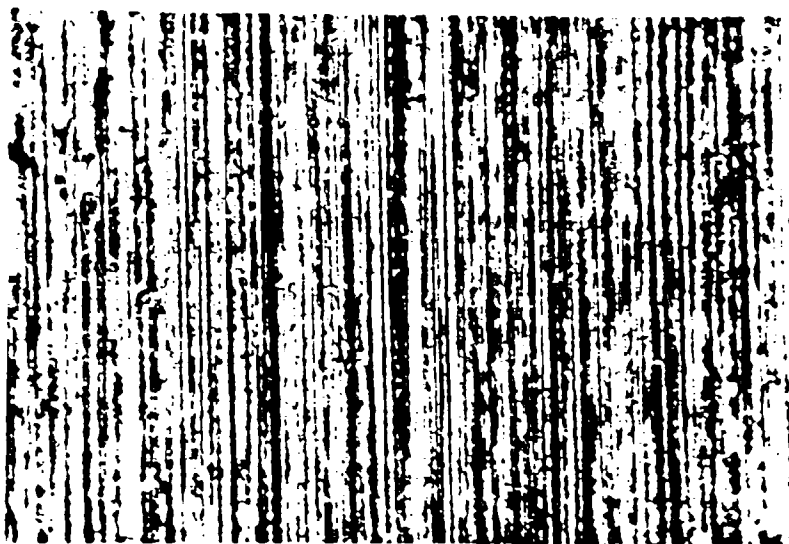
Figure 5.1.   Al 2024-T3 Before Pretreatment.
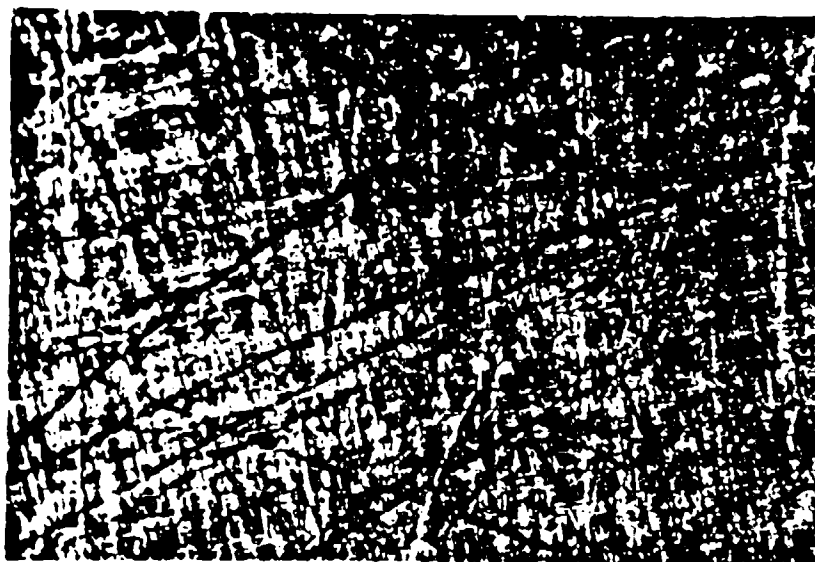
Figure 5.2.   Al 2024-T3 After WND-4 Pretreatment (Wetsanding by
                   Hand with Hydrolyzed Z-6040).
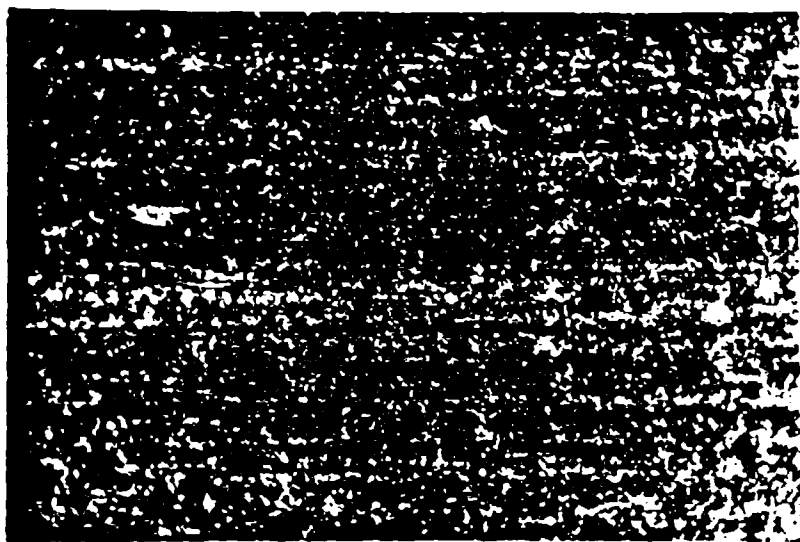
Figure 5.3.   Al-2024-T3 After FPL Etch Pretreatment.
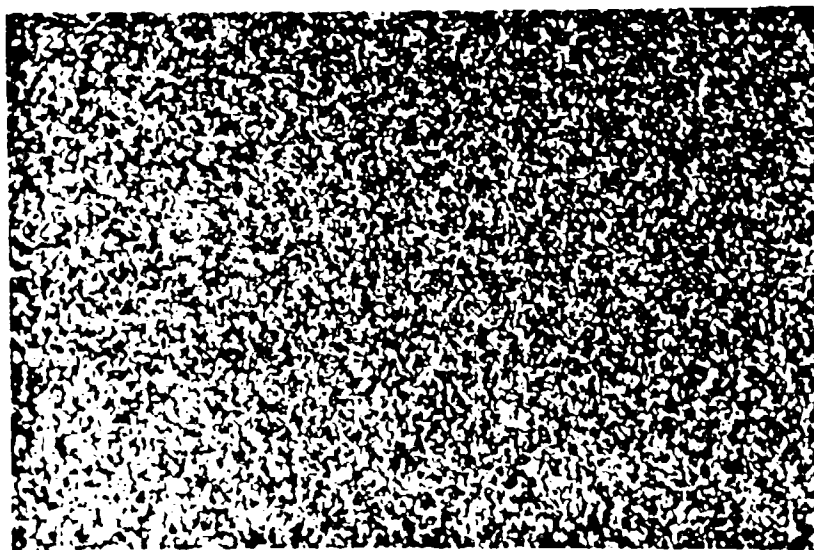
Figure 5.4.   Al-2024-T3 After High Pressure Water Blast
                Pretreatment (15 sec @ 5,000 psi, fine grit).

Figure 5.5.   Al-7075-T6 After High Pressure Water Blast
                   Pretreatment (30 sec @ 3,000 psi, fine grit).

The vapor honing technique appears to abrade the surface in a very uniform fashion, producing a finish
that resembles the FPL etched surface at low magnification. The high pressures employed in this
abrasion insure that the surface receives a high level of mechanical energy which is difficult to achieve by
the hand sanding method. Such a process would allow close control over process parameters such as
pressure, fineness of abrasives, and depth of the abrasion. The equipment used for this technique can
also be readily fitted with a chemical injector which would allow the addition of surface reactive agents
such as silane coupling agents to the water-abrasive medium. The development of this type of abrasion
methodology would be a logical next step in applying the pre-bond surface treatments identified in this
program to actual adhesive repair situations in the field.

6.0 CONCLUSIONS

The important conclusions of this study on the adhesive bonding of aluminum structures in the field are:

1) FPL etching was found to produce the largest changes in surface
    morphology of aluminum adherends and wetsanding by hand with
    hydrolyzed silanes had the least effect by SEM analysis. Alkali-
    silicate etching produced an intermediate effect.

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2)   Initial adhesive bond strength is relatively independent of
      pretreatments, primers and alloys employed.

3)   Adherend pretreatment plays a significant role in adhesive bond
      durability; FPL etching or wetsanding with aqueous solutions of
      3-glycidoxypropyltrimethoxysilane yielded hydrothermally stable
      bonds while etching with strong alkali or wetsanding with
      solutions of primers in organic solvents were not found to be as
      effective.

4)   Primers formulated with aromatic amine curing agents produce more
      durable adhesive bonds on wetsanded aluminum adherends than
      primers based on cycloaliphatic amine curing agents.

5)   Curing primers based on phosphate-modified epoxy-silicone
      copolymers at room temperature produces adhesive bonds with
      improved hydrothermal stability over samples where primers were
      first cured at elevated temperatures. Furthermore, adherends
      prepared by the WND-4 pretreatment method and primed with
      phosphate-modified epoxy-silicone resins yield adhesive bonds
      with comparable lap shear strength and durability to those
      prepared by the FPL process and commercial primers.

6)   The level of silicone resin in phosphate-modified, epoxy-silicone
      copolymer primers significantly affects the durability of
      adhesive bonds under hydrothermal stress. A 5-weight percent
      loading of polysiloxane was found to be optimum.

7)   The durability of adhesive bonds was found to be relatively
      insensitive to the size of the polysiloxane blocks used in the
      primer copolymer resins.

8)   The adhesive bond durability of specimens prepared with Al 7075-
      T3 was found to be highly dependent on surface pretreatment.
      Adhesive samples prepared by the FPL method and primed with

either experimental primer B2 or a commercial primer displayed excellent bond stability. Bonds prepared by the WND-4 method and primed with experimental primer B2 were found to be less stable to hydrothermal stress.

9) Adhesive bonds prepared on Al 2024-T3 by either the WND-4 pretreatment and experimental primer B2 or by FPL etch pretreatment and commercial primer showed equivalent durability when subjected to week-long immersion in water at $120^\circ F$ and $140^\circ F$.

7.0 RECOMMENDATIONS

The principal goal of this research program was to demonstrate the feasibility of using pre-bond surface treatments and experimental primers to prepare aluminum surfaces for strong, durable adhesive bonding. The process was designed for aircraft field repair operations and thus, should avoid the use of hazardous chemicals or complicated equipment. Primers based on phosphate-modified, epoxy-silicone copolymers were developed and tested in conjunction with different surface pretreatments. A series of experimental primer formulations were successfully employed over wetsanded adherends to yield adhesive bonds with strength and durability comparable to those prepared by the current state-of-the-art methods.

The condition of the adherend surface before priming was found to be an important variable for reproducibly forming durable bonds. Controlling the variables of the mechanical abrasion process such as pressure, depth of abrasion, abrasive grade, and duration of abrasion would be recommended for improving the reproducibility of the method as well as for increasing the scope of this adhesion technology. A portable, high-pressure water sandblaster would be a logical choice for this application. These units are available with chemical injectors for introducing waterborne agents such as silane adhesion promoters. Abrasion by the vapor honing technique could be performed in a very narrow time frame and on large parts. This may be an important consideration given the effects of hydrolysis time on the reactivity of silane coupling agents observed in this study.

Other recommendations for continued research include a comprehensive screening of the primer formulations which appeared promising in the Phase I program. The primer evaluation process would be greatly aided by the better controlled pretreatment conditions afforded by vapor honing. Formulation work would also be in order to develop the simplest and most cost effective primers for this application. Consideration should also be given to primer properties such as shelf life, compatibility with different

substrates and adhesives, and performance dependence on the purity of starting materials and concentration variations. Once the methodology for preparing and applying the pre-bond surface treatments has been developed and thoroughly tested, it may be transferred to the sponsor for further field evaluation. Feedback from field trials would be used to improve and further refine the technology.

8.0 REFERENCES

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3. T. J. Reinhart, "Surface Treatments for Bonded Repair of Metals", Chapter 2 in A. A. Baker and R. Jones, eds., *Bonded Repair of Aircraft Structures*, pp 23-29, Martinius Nijhoff Publishers, Boston, 1988

4. Smith, T., "Mechanisms of Bond Endurance after Surface Treatment of Aluminum for Bonding (STAB) in Nonchromate, Alkaline Solution, J.Adhesion, 14 145 (1982)

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6. W. Purcell, private communication

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APPENDIX 1

EFFECT OF TEMPERATURE ON PRIMER CURE RATE

——— FTIR-MIR spectrum of uncured primer

—·—·— FTIR-MIR spectrum of primer after curing for 60 minutes at 25 °C

— — — FTIR-MIR spectrum of primer after curing for 60 minutes at 60 °C
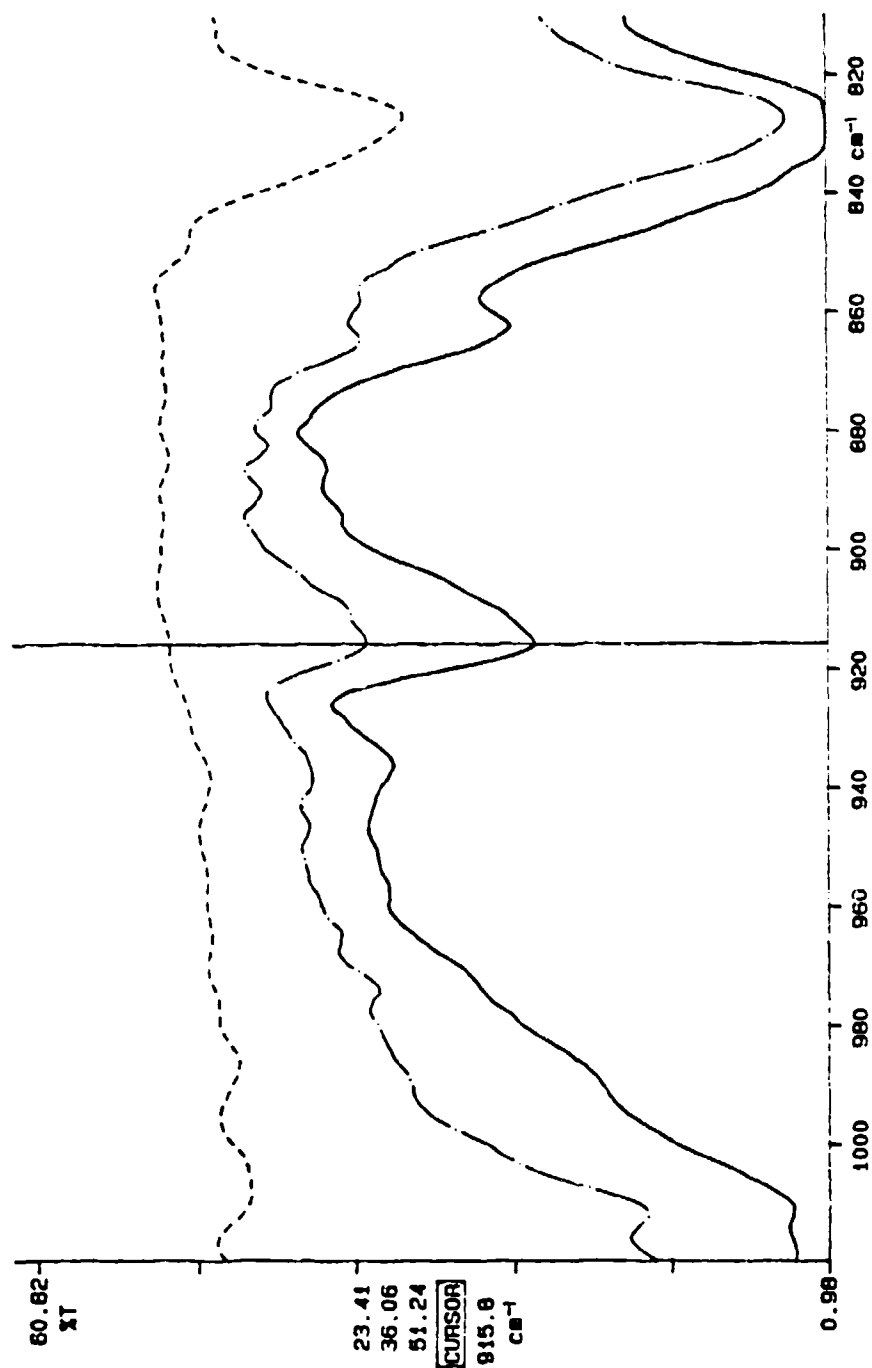
APPENDIX 1 (continued)

COHESIVE FAILURE WITHIN PRIMER OF LAP SHEAR SAMPLE 35
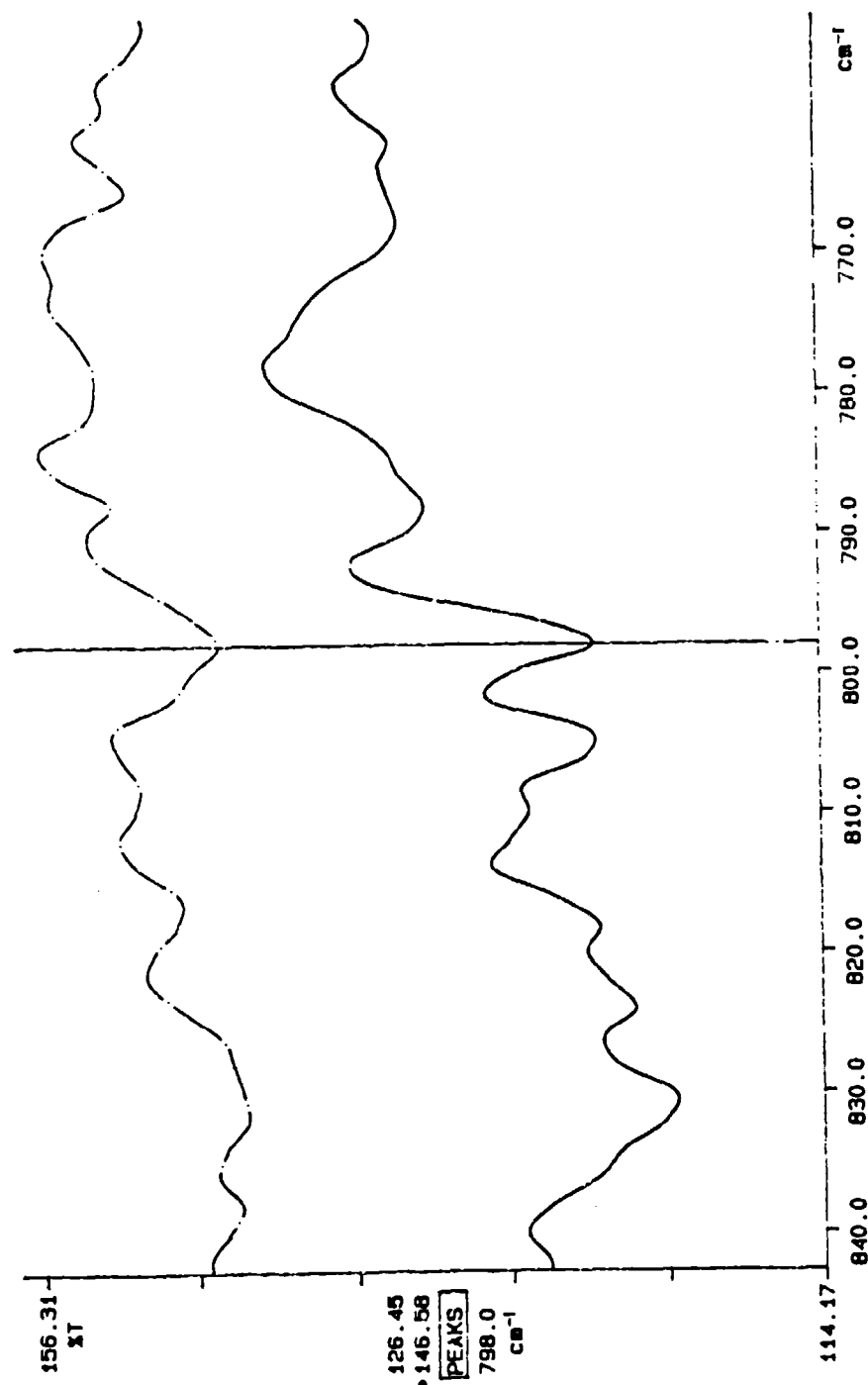
······ FTIR-MIR spectrum of failed adherend surface showing primer layer

―――― FTIR-MIR spectrum of failed adherend surface showing presence of primer layer on adhesive surface

ROOM TEMPERATURE WEDGE TEST RESULTS

Sample #	Primer Code	Pretreatment	Primer Cure Conditions min/C	Aluminum Alloy	Initial Crack Distance (in)	Standard Deviation	Crack Distance 1 hour (in)	Standard Deviation	Crack Distance 2 hours (in)
1	BR-127	FPL	30/120	2024-T3	1.41	.05	0.0	0	0.01
2	A1	WND-1	60/65	2024-T3	1.9	.2	0.7	.1	0.8
3	A2	WND-2	60/65	2024-T3	2.2	.2	0.3	.1	0.6
14	A1	SIL-1	60/65	2024-T3	2.1	.4	1.0	.2	1.4
22	A3	SIL-2	60/65	2024-T3	2.0	.3	2.0	.2	2.2
23*	A3	WND-4	60/65	2024-T3	1.4	.1	0.2	.4	0.3
7	B5	WND-4	50/65	2024-T3	1.8	.3	0.3	.2	0.4
35b	B2	WND-4	60/25	2024-T3	1.56	.05	0.0	0	0.0
25	B8	WND-4	60/65	2024-T3	1.3	.1	0.03	.04	0.04
24*	A3	WND-3	60/65	2024-T3	1.8	.3	0.4	.2	0.6
26*	D1	WND-4	60/65	2024-T3	1.47	.03	0.05	.06	0.1
29*	B9	WND-4	60/65	2024-T3	1.49	.05	0.03	.02	0.04
28	B6	WND-4	60/65	2024-T3	1.47	.05	0.02	.03	0.04
27	B1	WND-4	60/65	2024-T3	1.44	.02	1.2	.3	1.4
35	B2	WND-4	60/65	2024-T3	1.5	.1	0.0	0	0.02

Sample #	Standard Deviation	Crack Distance 4 hours (in)	Standard Deviation	Crack Distance 24 hours (in)	Standard Deviation	Crack Distance 48 hours (in)	Standard Deviation	Crack Distance 168 hours (in)	Standard Deviation
1	.02	0.01	.02	0.01	.02	---	---	0.01	0.01
2	.2	1.0	.2	1.4	.3	1.5	.3	---	---
3	.1	0.7	.1	1.4	.3	1.5	.3	---	---
14	.2	1.7	.4	2.4	.6	---	---	---	---
22	.3	2.2	.3	2.3	.3	2.3	.3	---	---
23*	.4	0.4	.4	0.5	.4	0.5	.4	0.7	.1
7	.2	0.5	.2	0.7	.1	---	---	---	---
35b	0	0.0	0	0.01	.01	---	---	0.02	.02
25	.04	0.06	.03	0.07	.02	0.09	.03	0.15	.06
24*	.2	0.6	.2	0.8	.2	---	---	1.0	.3
26*	.1	0.1	.2	0.3	.3	---	---	0.7	.3
29*	.03	0.06	.04	0.09	.03	---	---	0.11	.03
28	.03	0.04	.04	0.08	.03	---	---	0.14	.04
27	.2	1.7	.2	1.8	.2	---	---	2.0	.2
35	.03	0.02	.04	0.06	.05	---	---	0.25	.08

* Average of four samples
** Average of two samples

APPENDIX 2 (continued)

ROOM TEMPERATURE WEDGE TEST RESULTS

Sample #	Primer Code	Pretreatment	Primer Cure Conditions min/C	Aluminum Alloy	Initial Crack Distance (in)	Standard Deviation	Crack Distance 1 hour (in)	Standard Deviation	Crack Distance 2 hours (in)
32	NA	WND-4	NA	2024-T3	1.6	.1	1.4	.4	1.8
34	B7	WND-4	60/65	2024-T3	2.0	.6	0.07	.07	0.12
34**	B7	WND-4	60/65	2024-T3	1.43	.04	0.01	.01	0.02
15	C1	WND-4	60/65	2024-T3	4.0	.4	0.11	.03	0.14
15b*	C1	WND-4	60/25	2024-T3	1.51	.08	0.03	.03	0.04
6	B4	WND-4	60/25	2024-T3	1.7	.1	0.3	.1	0.3
8*	S10	WND-4	60/25	2024-T3	1.8	.3	0.01	.02	0.01
34b*	B7	WND-4	60/25	2024-T3	2.0	.4	0.06	.06	0.1
7b*	B5	WND-4	60/25	2024-T3	1.49	.09	0.0	.01	0.0
5	B3	WND-4	60/25	2024-T3	3.0	.3	0.04	.02	0.06
76	B2	FPL	60/25	2024-T3	1.41	.02	0.0	0	0.0
85	B2	FPL	60/25	7075-T6	1.49	.04	0.0	0	0.0
48	BR-127	FPL	30/120	7075-T6	1.46	.03	0.0	0	0.0
50	B2	WND-4	60/25	7075-T6	1.9	.2	0.40	.07	...
58	B11	WND-4	60/25	7075-T6	1.38	.02	...	...	...

Sample #	Standard Deviation	Crack Distance 4 hours (in)	Standard Deviation	Crack Distance 24 hours (in)	Standard Deviation	Crack Distance 168 hours (in)	Standard Deviation
32	.3	2.2	.3	2.8	.2	3.2	.2
34	.09	0.12	.09	0.2	.1	0.2	.1
34**	.03	0.02	.03	0.07	.02	0.08	.02
15	.05	0.18	.06	0.23	.06	0.3	.1
15b*	.05	0.06	.06	0.06	.08	0.2	.1
6	.1	0.4	.2	0.4	.2	0.5	.2
8*	.02	0.02	.02	0.02	.02	0.03	.03
34b*	.1	0.1	.1	0.1	.1	0.1	.1
7b*	.01	0.0	.01	0.01	.02	0.04	.03
5	.03	0.06	.03	0.10	.03	0.09	.06
76	0	0.0	0	0.0	0	0.03	.03
85	0	0.0	0	0.0	0	0.04	.04
48	0	0.01	.02	0.05	.03	0.07	.04
50	...	...	...	...	...	0.52	.08
58	...	...	...	...	...	...	...

* Average of four samples
** Average of two samples

43

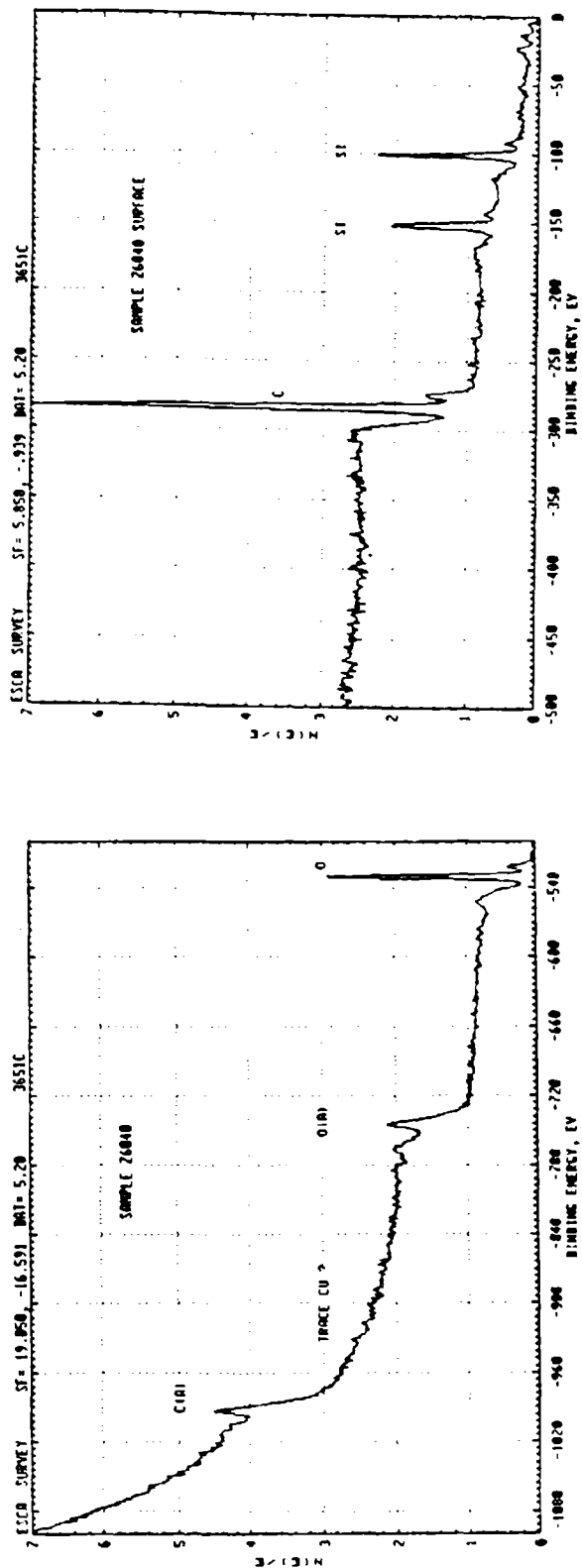## ELEVATED TEMPERATURE WEDGE TEST RESULTS

Sample #	Primer Code	Pretreatment	Primer Cure Conditions min/C	Aluminum Alloy	Immersion Temperature (F)	Initial Crack Distance (in)	Standard Deviation	Crack Distance 1 Hour (in)	Standard Deviation
40*	B2	WND-4	60/25	2024-T3	120	1.54	.06	0.04	.04
40*	B2	WND-4	60/25	2024-T3	140	1.54	.06	...	...
42*	BR-127	FPL	30/120	2024-T3	120	1.42	.03	0.01	.01
42*	BR-127	FPL	30/120	2024-T3	140	1.42	.03	...	...

Sample #	Crack Distance 2 hours (in)	Standard Deviation	Crack Distance 4 hours (in)	Standard Deviation	Crack Distance 24 hours (in)	Standard Deviation	Crack Distance 168 hours (in)	Standard Deviation
40*	0.07	.03	0.08	.03	0.10	.04	0.12	.03
40*	0.18	.04	0.19	.04	0.23	.03	0.45	.06
42*	0.01	.01	0.04	.03	0.10	.03	0.16	.03
42*	0.19	.03	0.20	.03	0.24	.03	0.39	.03

* Average of four samples

APPENDIX 3

ESCA ANALYSIS OF ALUMINUM ALLOY 2024 AFTER WETSANDING WITH HYDROLYZED Z-6040 SOLUTION

PICK NEXT POINT
9458, -71.200
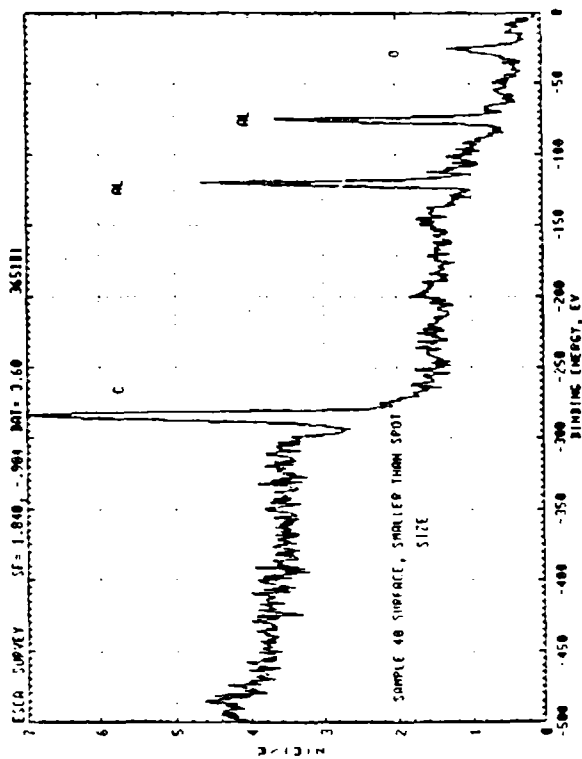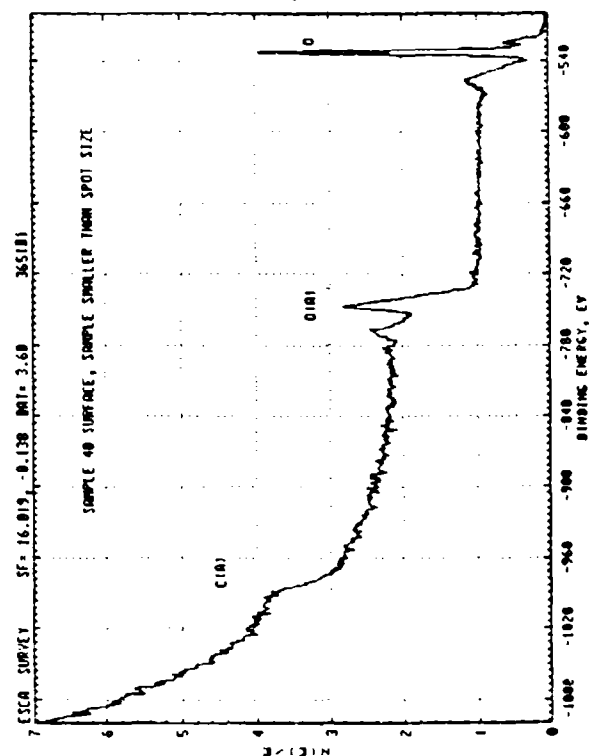
AREA SENSITIVITIES:

C 1   53.9
O 1   30.0
SI1   15.7
Al 1   0.2

>SAMPLE Z6040 SURFACE

APPENDIX 3 (continued)

ESCA ANALYSIS OF FAILED ELEVATED TEMPERATURE WEDGE

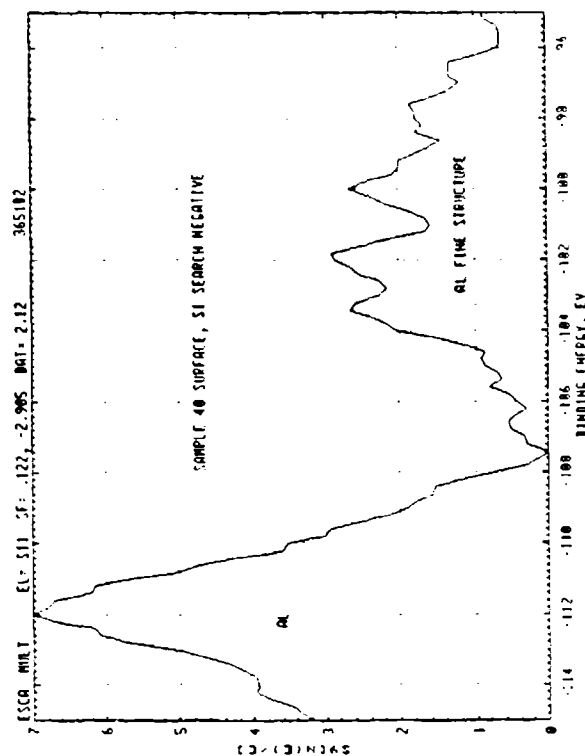## TEST SAMPLE #40 FOCUSING ON DEBONDED REGION
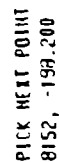

PICK NEXT POINT
32386, -589.800

AREA SENSITIVITIES:

C 1   29.8
O 1   53.4
AL1   16.6
S11   ****
CR1   ****

>SAMPLE 40 SURFACE

APPENDIX 3 (continued)

ESCA ANALYSIS OF FAILED ELEVATED TEMPERATURE WEDGE
TEST SAMPLE #42 FOCUSING ON DEBONDED REGION

PICK NEXT POINT
8152, -198.200

AREA SENSITIVITIES:

C 1   7.4
O 1   69.4
AL1   22.9
CL1   0.1

>SAMPLE 42 SURFACE